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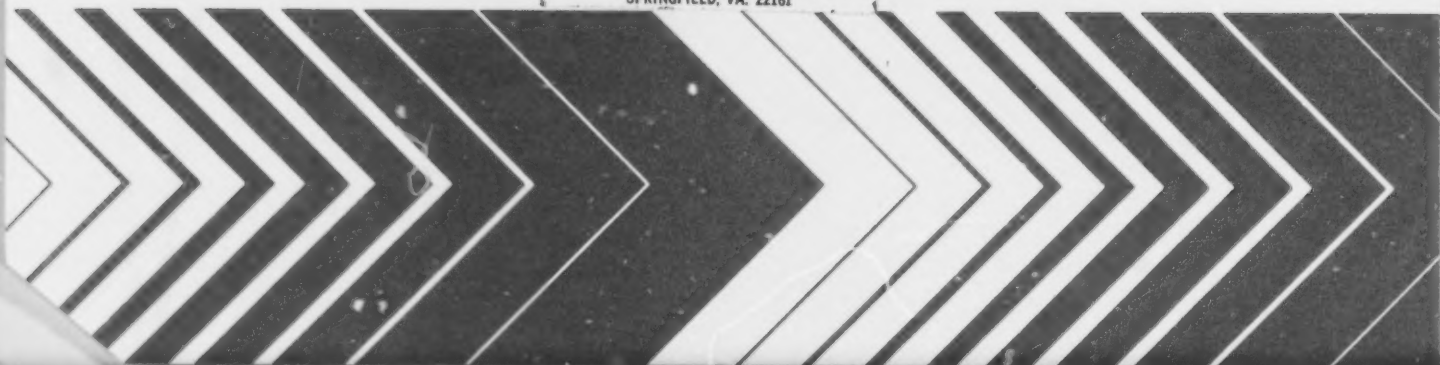
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Trace Element Study at a Primary Copper Smelter

Volume I

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TRACE ELEMENT STUDY AT
A PRIMARY COPPER SMELTER

Volume I

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents the findings of an investigation of air pollutant emissions from the reverberatory furnace pollution control system at a primary copper smelter. The study was performed to assess the degree of particulate emissions control and control problems associated with the application of electrostatic precipitators in the nonferrous metals production industry. The results are being used within the Agency's Office of Research and Development as part of a larger effort to define the potential environmental impact of emissions from this industry segment and the need for improved controls. The findings will also be useful to other Agency components and the industry in dealing with environmental control problems. The Metals and Inorganic Chemicals Branch of the Industrial Pollution Control Division should be contacted for any additional information desired concerning this program.

David C. Stephan
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ABSTRACT

The present study was sponsored by the Industrial Environmental Research Laboratory of EPA, Cincinnati. It describes results obtained by sampling at a primary copper smelter with a production rate of 200 tons Cu/day. Concentrate, matte and slag streams of the reverberatory furnace were analyzed. The main effort of the study, however, focused on the electrostatic precipitator (ESP) controlling particulate emissions from the reverberatory furnace. The main findings of the study are presented below.

SMELTER MINOR ELEMENT FLOW

- 1) Titanium, potassium, magnesium, and sodium enter the smelter as major components besides the elements of importance in the smelting operation itself (Cu, Fe, Si, Ca, and Al).
- 2) Minor elements of environmental concern are:
 - arsenic,
 - cadmium,
 - molybdenum,
 - lead,
 - antimony,
 - selenium,
 - zinc, and
 - fluorine.
- 3) The rest of the elements surveyed enter in the low ppm concentration range or were not detected by spark source mass spectrometry analysis.
- 4) Molybdenum entering the reverberatory furnace with the concentrate is almost completely discharged in the reverberatory furnace slag.
- 5) Nearly 50 percent of the selenium and 30 percent of the fluorine are discharged together with the reverberatory furnace off-gases.
- 6) Nearly all of the fluorine escapes in the gaseous state.

ARSENIC SAMPLING

The arsenic flows found by Radian have been compared in this report to tests made by smelter personnel during the periods of February 28 through March 4, 1977. In addition, integral arsenic balances were established for the months of January and March 1977 from the plant data. The findings are incorporated in this report.

- 1) Approximately 50 percent of the arsenic entering the smelter leaves in the reverberatory furnace off-gas based on both plant and Radian sampling data.
- 2) Data gathered during this sampling study indicate that as much as 90 percent of the arsenic entering the reverberatory furnace ESP may leave in the off-gas.
- 3) Arsenic and selenium escaping the electrostatic precipitator are partly in the vapor state.
- 4) The arsenic concentration in the reverberatory furnace feed varies within a few days from 700 ppm to 7000 ppm. This variation is not only a function of the arsenic concentration in the ore, but also depends on the amount of electrostatic precipitator dust recycled.
- 5) The following arsenic rates were determined at the ESP outlet:
 - 140 lb/hr - July 11, 1976 - Radian, direct measurement
 - 76 lb/hr - July 13, 1976 - Radian, direct measurement
 - 54 lb/hr - July 13, 1976 - Radian, direct measurement
 - 45 lb/hr - July 14, 1976 - Radian, direct measurement
 - 51 lb/hr - July 14, 1976 - Radian, direct measurement
 - 45 lb/hr - January, 1977 - Smelter, balance difference
 - 40 lb/hr - March, 1977 - Smelter, balance difference
 - 25 lb/hr - March 1, 1977 - Smelter, direct measurement
 - 34 lb/hr - March 2, 1977 - Smelter, direct measurement
 - 49 lb/hr - March 3, 1977 - Smelter, direct measurement
- 6) The arsenic detected was present as arsenolite, As_2O_3 . This was determined by X-ray diffraction.

ESP PERFORMANCE

- 1) ESP temperature (600°F) and gas flow rate (160,000 acfm) correspond to design parameters.
- 2) ESP inlet grain loading determined at duct temperature is 0.60 grains/scf, and the outlet grain loading is 0.020 grains/scf. The overall particulate collection efficiency is calculated to be 96.7%. Design efficiency was 96.8%.
- 3) The amount of condensibles between duct temperature 600°F and 250°F (EPA recommended) accounts for material corresponding in mass to an additional 1.60 gr/scf at the inlet and 1.0 gr/scf at the outlet.
- 4) The element flow at the reverberatory furnace ESP outlet measured July 11, 1976 is as follows:

Sulfur	2260	lbs/hr
Arsenic	140	lbs/hr
Fluorine	7.8	lbs/hr
Copper	1.0	lbs/hr
Selenium	.97	lbs/hr
Antimony	.33	lbs/hr
Molybdenum	.2	lbs/hr
Nickel	.1	lbs/hr
Lead	.1	lbs/hr
Zinc	.1	lbs/hr

- 5) Good material balance closure around the ESP was established for:

Arsenic	Nickel
Beryllium	Sulfur
Chromium	Antimony
Copper	Selenium
Fluorine	Vanadium
Mercury	Zinc
Molybdenum	

The balance for cadmium is marginal. The balance for barium and lead did not close due to precipitation of insoluble sulfates in the collection device.

- 6) Cadmium, lead, and zinc entering the smelter are transported with the matte to the converters. Cadmium most likely leaves the smelting circuit with the converter off-gases. Some of the zinc and lead will be volatilized in the converter. Some will also be returned to the reverb in the converter slag.

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SECTION 1

INTRODUCTION

The primary copper smelter studied in this report started production about 25 years ago. Gas cleaning facilities were added in the early seventies to treat the off-gases from the converters. Waste heat boilers and electrostatic precipitators are currently used to generate steam and remove particulates from both reverberatory furnace and converter gas streams. The cleanup and cooling of converter gases is achieved in a humidifier, cooler, wet electrostatic precipitator arrangement followed by a contact sulfuric acid plant.

The primary goal of the present study was to evaluate the performance of the electrostatic precipitator collecting particulate matter escaping the reverberatory furnace. Several sampling techniques were chosen to determine:

- gas flow rate,
- gas composition,
- grain loading at the inlet duct,
- grain loading at the outlet duct,
- particle size distribution,
- electrical performance of the ESP,
- trace element material balance,
- trace element flow rates as vapor,
- the amount of material condensible between the gas temperature of 600°F and the EPA recommended cool-off point of 250°F, and
- arsenic emission rates using an EPA suggested sampling device.

The sampling effort was conducted from July 8 through July 16, 1976. A detailed sampling schedule is presented in Table 1-1.

TABLE 1-1. A SUMMARY OF THE SAMPLING EFFORT
(JULY 7 THROUGH JULY 16, 1976)

Date	Location/Stream Sampled	Parameter	Technique
Evaluate Reverb ESP performance:			
7-8 to 7-10	ESP Outlet	grain loading	in-stack filter
7-10	ESP Outlet	particle size distribution	Andersen cascade impactor (SRI)
7-8 to 7-10	ESP Inlet	grain loading	in-stack filter
7-10	ESP Inlet	particle size distribution	Brink cascade impactor (SRI)
7-10	ESP Control Room	electrical performance	monitor operating parameters (SRI)
Complete a material balance around Reverb ESP:			
7-11	ESP Outlet	trace element flow rates	Integral WEP
7-11	ESP Inlet	trace element flow rates	Integral WEP
7-11 to 7-13	ESP Dust	trace element flow rates	periodic grab sample
Complete an approximate material balance around the Reverb furnace:			
7-13	ESP Outlet	trace element flow rates	Integral WEP
7-12 to 7-14	Reverb feed	trace element flow rates	compositing slinger bin catches at the end of each shift
7-11 to 7-13	ESP Dust	trace element flow rates	periodic grab sample
7-12 to 7-14	Reverb Slag	trace element flow rates	periodic grab sample
7-12 to 7-14	Matte	trace element flow rates	periodic grab sample
Collect particulate by particle size for trace element analysis:			
7-16	ESP Outlet	particulate by size fraction	3 out of stack cyclones in series plus filter
Collect vapor phase emissions:			
7-16	ESP Outlet	trace element flow rates as vapor	filter at duct temperature followed by Impingers
Determine amount of condensible material and SO _x emitted:			
7-15	ESP Outlet	condensed material (between 600°F-250°F) and SO ₂ -SO ₃ concentrations	EPA 5 train with in-stack filters
7-15	ESP Outlet	condensed material (between 600°F-250°F) and SO ₂ -SO ₃ concentrations	EPA 5 train with in-stack filters
Determine arsenic emission rates:			
7-13 to 7-14	ESP Outlet	arsenic emission rate	modified EPA Method 5 train
7-13 to 7-14	ESP Inlet	arsenic emission rate	modified EPA Method 5 train

Plant management released composites of the following samples:

- concentrate (reverberatory furnace feed),
- matte, and
- reverberatory furnace slag.

In addition, all critical flow rates were released to Radian. A complete material balance around the reverberatory furnace was still not possible because compositions for the following streams are not known:

- converter slag,
- dust collected in the converter waste heat boiler, balloon flue, and ESP, and
- material condensed on the surface of the reverberatory furnace waste heat boiler.

The study was performed in parallel with an effort by Southern Research Institute, Birmingham, Alabama (SRI). SRI determined the electrical characteristics of the ESP during the sampling period and also determined the particle size distribution at the inlet and outlet using Brink's impactors. Details of these investigations can be found in SRI's report: "Performance Evaluation of an Electrostatic Precipitator Installed on a Copper Reverberatory Furnace," SORI-EAS-76-511, EPA Order No. CA-6-99-2980-J.

The important results and conclusions are summarized in this volume of the report. Descriptions of the smelter, the reverberatory furnace, and the electrostatic precipitator are presented in Section 2. Section 3 describes the sampling techniques used to perform each experiment listed in Table 1-1.

Section 4 presents the data generated by this study. The results and data limitations are also explained in this section. More detailed descriptions of the sampling and analytical procedures are presented in Volume II along with the actual sampling data.

SECTION 2

PLANT DESCRIPTION

This section first presents a general process description of the smelter studied. The reverberatory furnace and the hot electrostatic precipitator are described next. The plant operation during the sampling program is covered last.

MATERIAL FLOW

The primary copper smelter studied in this report started production about 25 years ago. Gas cleaning facilities were added in the early seventies to treat the off-gases from the converters. The copper smelting facility sampled can be divided into the following process steps (see Figure 2-1):

- mining,
- concentrate preparation,
- reverberatory furnace feed preparation,
- matte production in the reverberatory furnace,
- production of blister copper in the converters and copper refining in the anode furnace, and
- cleaning of the converter off-gases with sulfuric acid production.

An open pit mine feeds the smelter. Typical copper concentrations in the ore range from 0.5 to 1.0%. All ore with less than 0.3% copper content is rejected as waste rock.

The process flow is depicted in Figures 2-2 and 2-3. Several trains transport the ore from the mine to the crushing and grinding unit. The first step is the reduction of the larger boulders in a gyratory crusher. Continuous reduction of the rock size is achieved first in cone crushers than finally in wet ball mills.

The smelter uses a conventional flotation process. Water and flotation reagents are added to the ball mill effluent stream and the slurry is aerated. Copper bearing particles adhere to the ascending air bubbles. The "froth" is

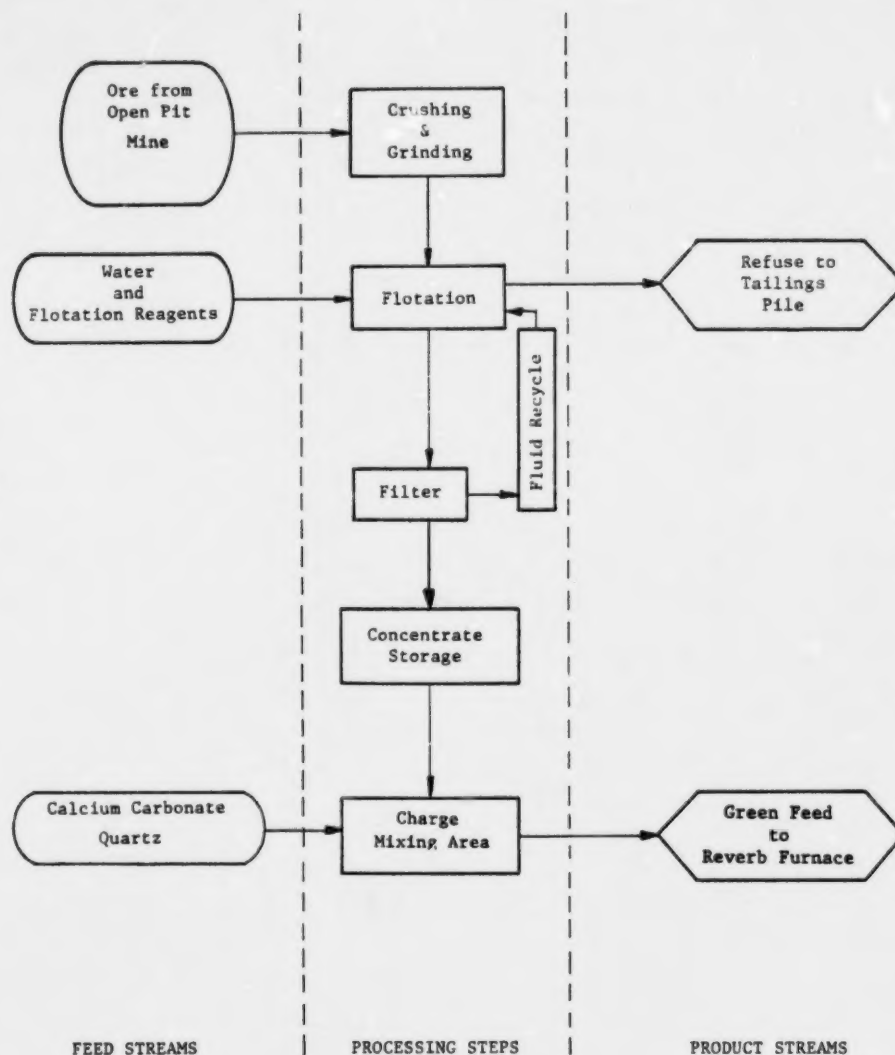


Figure 2-2. Reverberatory Furnace Feed Preparation.

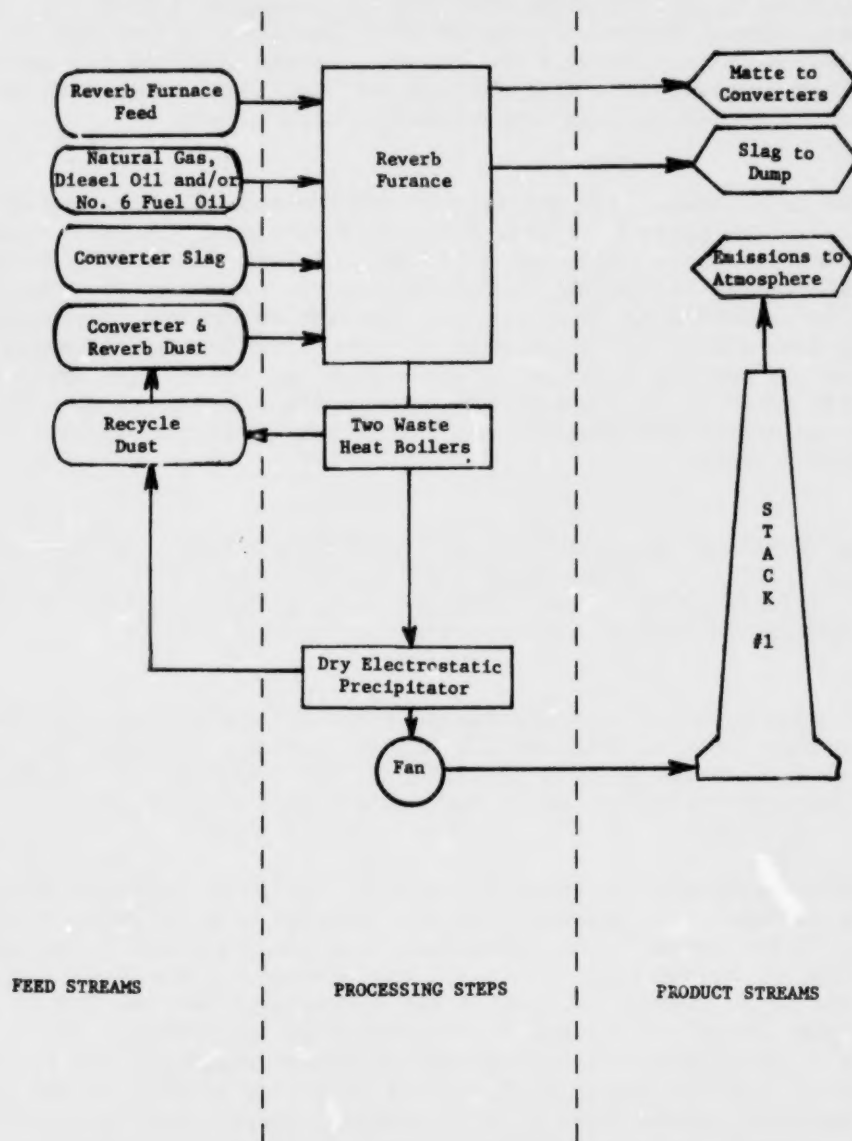


Figure 2-3. Reverberatory Furnace Flow Diagram.

skimmed from the surface. Solid-liquid separation is achieved next by vacuum filtration. The aqueous phase is recycled, and the concentrate containing 20% or more copper goes to storage. The particulates low in copper ore sink to the bottom in the flotation step and are pumped as a slurry to the tailings pond. Again, supernatant water from this pond is recycled to the ore enrichment facility. The ore and concentrate are analyzed for copper, and major constituents. Calcium carbonate and quartz are mixed with the concentrate to produce an optimum reverberatory furnace feed.

The major steps in operating the reverberatory furnace are shown in Figure 2-3. The purpose of this furnace is to reduce the sulfur and iron in the concentrate to the point where FeS and Cu_2S are present in approximately stoichiometric amounts. This mixture is called matte. Excess iron sulfide is converted in an exothermic reaction to FeO and SO_2 . Iron oxide combines with silica to form a slag of lower density than the matte. The slag layer is removed from the reverberatory furnace and transported in a slag train to the slag dumping site. The off-gases contain sulfur dioxide, particulate matter and fumes of metal compounds. Heat is recovered in two waste heat boilers.

Particulates are removed in two waste heat boilers and in a hot electrostatic precipitator. These collected dusts are recycled to the reverberatory furnace feed preparation area. The gas leaving the reverb ESP is discharged to the atmosphere through the reverberatory furnace stack.

Streams entering the reverberatory furnace in addition to the concentrate (reverb furnace feed) are (1) converter slag, (2) converter dusts collected in both the balloon flue and the ESP treating the converter off-gases, and (3) reverb ESP and reverb waste heat boiler dusts.

Three Peirce-Smith converters process the matte produced in the reverberatory furnace. The schematic of the material flow is shown in Figure 2-4. Charging of the matte to the converters is a batch process using ladles transported by an overhead crane. In the converter, iron sulfide is oxidized to FeO and SO_2 . Quartz addition to the converter binds the FeO in the form of a silicate slag (4% Cu) which is recycled to the reverb. Again, the operation is discontinuous and is carried out using ladles and the overhead crane. "White metal" consisting of Cu_2S is left after the removal of the iron. At this stage, the copper blowing cycle starts. Copper sulfide is converted to a 98% pure copper called "blister copper". Cold copper-containing scrap is added periodically to absorb the heat of the exothermic reaction.

The blister copper is transported to the anode furnace using ladles. Air blowing serves to remove the sulfur left in the blister copper. Copper containing Cu_2O as an impurity is the result of this processing step. The

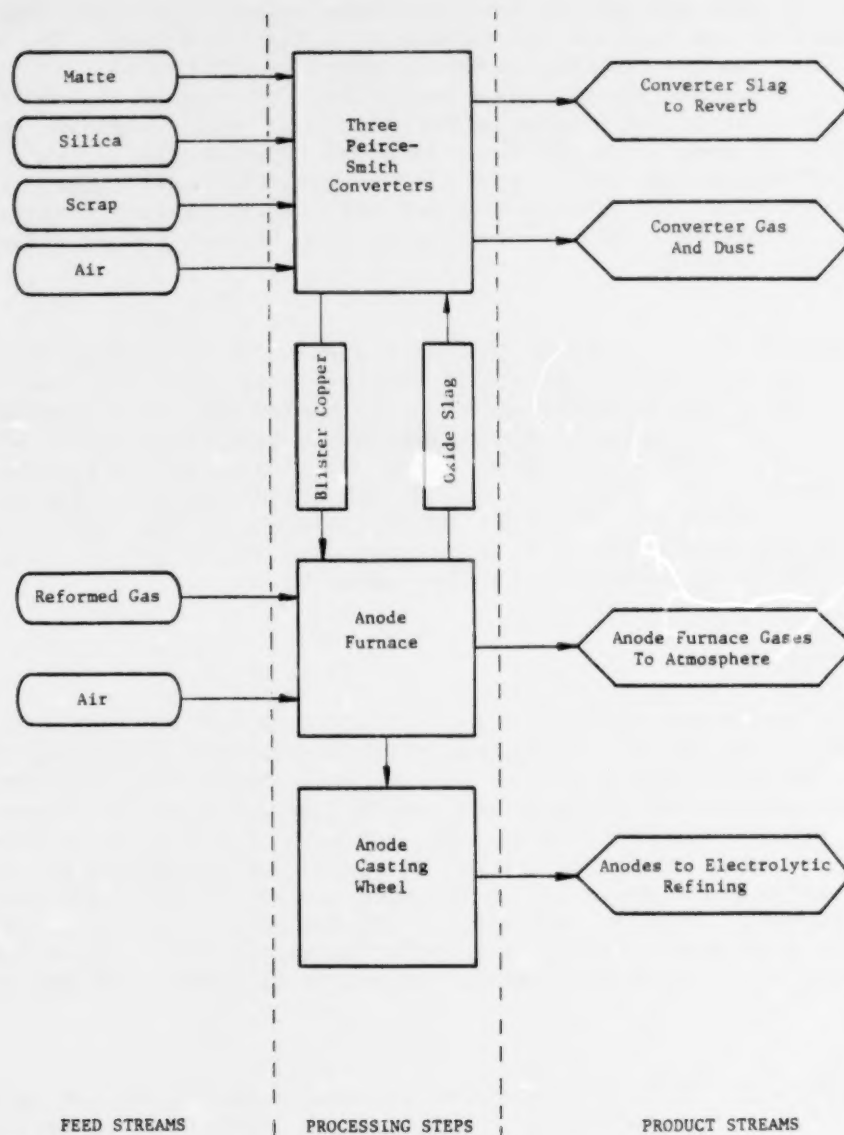


Figure 2-4. Converters and Anode Furnace.

copper oxide is then reduced with reformed gas. The resulting copper with a purity of 99+% is ready for the anode pouring step which is done once a day. An anode casting wheel is used. The anodes weigh about 750 lbs apiece and are shipped for electrolytic refining. Output of the plant is 180-200 tons of anode copper a day.

Sulfur dioxide off-gas and dust and fumes composed of metal compounds are the result of the Cu_2S and FeS oxidation in the converters. The converter dust collection and gas cleaning steps are shown in Figure 2-5. The SO_2 concentration of the converter off-gases varies between 4 and 8 percent (v) and as such is amenable to the manufacturing of sulfuric acid using the contact process. The off-gases from the converters are first cooled in waste heat boilers. Particulate removal is achieved in an electrostatic precipitator. The dust collected in the balloon flue and the electrostatic precipitator is recycled to the reverberatory furnace. Dust from the waste heat boilers is fed back to the converters.

Gas cooling and cleaning is the first step in sulfuric acid production. A humidifier, a cooler and a wet electrostatic precipitator are used to cool and clean the gas. The humidifying tower has a blowdown stream consisting of dilute sulfuric acid containing the particulate matter escaping the ESP, as well as condensable fumes. The H_2SO_4 plant consists of drying towers, a vanadium pentoxide catalytic bed, and SO_3 absorption towers. Heat exchangers remove the heat of the exothermic SO_2 oxidation process. The product of the sulfuric acid plant is a 93% H_2SO_4 acid stream and a tail gas with low (presently unknown) concentrations of contaminants.

REVERBERATORY FURNACE

The single reverberatory furnace, 30 feet wide and 100 feet long (inside dimensions), fired with burners which are capable of burning natural gas, diesel oil and/or No. 6 fuel oil, processes concentrates from the milling and flotation plant. The concentrates, which comprise over 90% of the furnace charge are received from the filter plant and dryer by conveyor or from stock piles by truck. Each charge is weighed on scales and is carried by overhead crane to a charge point above and to the side of the furnace. Six charge ports are provided, three on each side of the furnace. A concrete bin of approximately 1600 tons capacity is used for surge storage of concentrates. When necessary, the concentrates are reclaimed by clamshell from the storage bin.

The bath smelting reverberatory furnace was designed for wet (green charge) smelting. The crucible of the furnace is constructed in sections of rammed periclase. The top and sides of the furnace crucible are cooled by

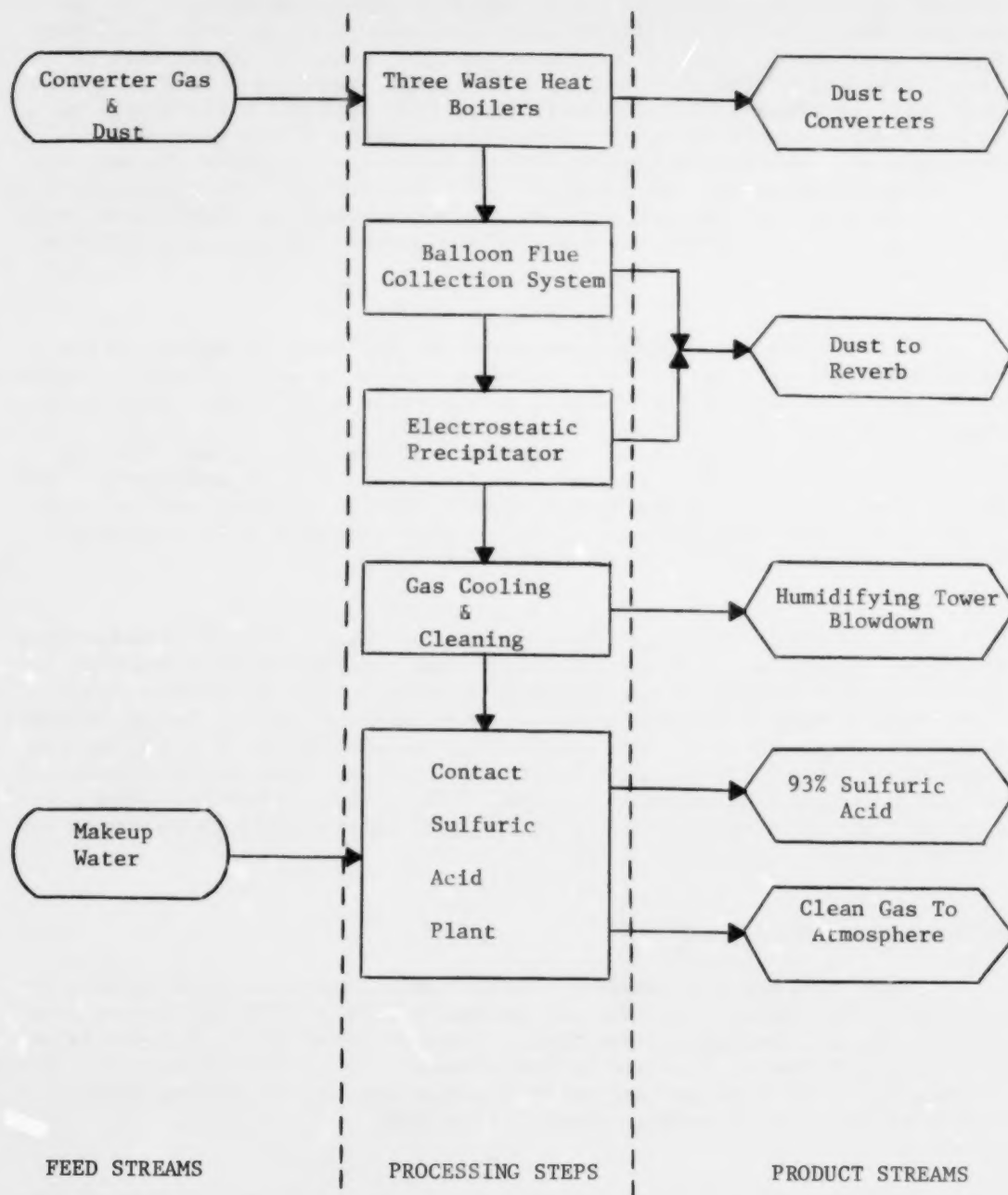


Figure 2-5. Converter Dust Recovery and H₂SO₄ Plant.

copper water jackets. The working bottom of the furnace is magnetite accretions fused in place. The bath smelting furnace requires reaction between the new charge and the liquid bath to cause spreading of the new charge. When calcines are smelted, charging them through an inclined pipe imparts sufficient velocity to allow a reaction with the liquid bath to cause spreading of the new charge. This gravity charging method cannot be used with wet concentrates, however, since they will not flow through an inclined pipe as will calcines. Considerable research was necessary to develop proper charging equipment. It is necessary to charge the wet concentrates to the furnace at a considerable velocity and at a relatively flat angle. This enables the wet concentrate to penetrate the liquid bath sufficiently to start the spreading reaction and prevents the concentrate from piling up in one place.

A high-speed belt slinger was developed for this operation and has performed well. Six slingers are provided, three on each side of the furnace. Each has a port through the sidewall covered with a vertically movable door when not in use. When charging begins, the door is raised by an air cylinder, the slinger started, and the concentrates drop onto the slinger from the charge can overhead. The slinger angle is adjustable both horizontally and vertically. Belt speeds are variable, allowing the charging rate to range from 1.5 to 2 tons/min for each slinger. Furnace charging is done by one man and is controlled by visual inspection.

The reverb is a sprung silica arch type. The brickwork is maintained by silica slurry hot patching. The silicious material of over 90% SiO_2 is ground wet in a ball mill and pumped to a storage tank above the furnace from which it is blown and sprayed onto the interior surface of the brickwork. A curtain damper has been used successfully in the furnace and its use has resulted in better working conditions and decreased maintenance expense in and around the boiler uptakes and flues. The curtain damper sections are made of cast refractory supported by loops of water-cooled steel tubing and are maintained by slurry patching.

REVERBERATORY FURNACE ESP

Gases from the reverberatory furnace enter two waste heat boilers in parallel. The boilers cool the gas to approximately 600°F and remove some particulate and condensable material. Steam produced by the boilers is used to generate either electricity or low-pressure air for the converters. Gases exiting the waste heat boilers enter a plenum chamber for mixing prior to treatment in an electrostatic precipitator (ESP).

The reverberatory furnace electrostatic precipitator consists of two independent horizontal parallel units designed to handle a total 160,000 acfm (600°F and 13.8 psia). Gas treatment time is 6 seconds; pressure drop across

the precipitator is 0.5 inches w.c. maximum. Collecting surfaces are plates; the discharge electrodes are spring steel wires. The transformer-rectifiers are silicon full wave for 45KV (DC) average; there is an automatic voltage control system to maintain the optimum precipitator operating efficiency. Dust collected is transported via screw conveyor and chain drag to a storage bin from which it is pneumatically conveyed to the charge mixing area for the reverberatory furnace by a fluid flow automatic pump. This pump can handle 20,000 pounds per hour when supplied with 280 scfm compressed air at 30 psig. The electrostatic precipitator and dust handling system are shown schematically in Figure 2-6.

An induced draft fan was installed to draw the reverberatory gases from the reverberatory furnace through the waste heat boilers, the flue system, and the electrostatic precipitator. This fan can handle 160,000 acfm @ 600°F with a suction of -1.75" H₂O and a discharge of 3.25" H₂O. The gases are discharged through a 360-foot concrete stack.

PLANT OPERATION DURING SAMPLING

The reverberatory furnace operated continuously during the entire sampling program. One upset in the ESP operation was recorded on July 12. This upset was attributed to wet concentrate charged to the furnace. The concentrate dryer was repaired that day and no further upsets were recorded. High dust loadings were noted during the periods when the reverberatory furnace was being charged. This, however, is normal operation.

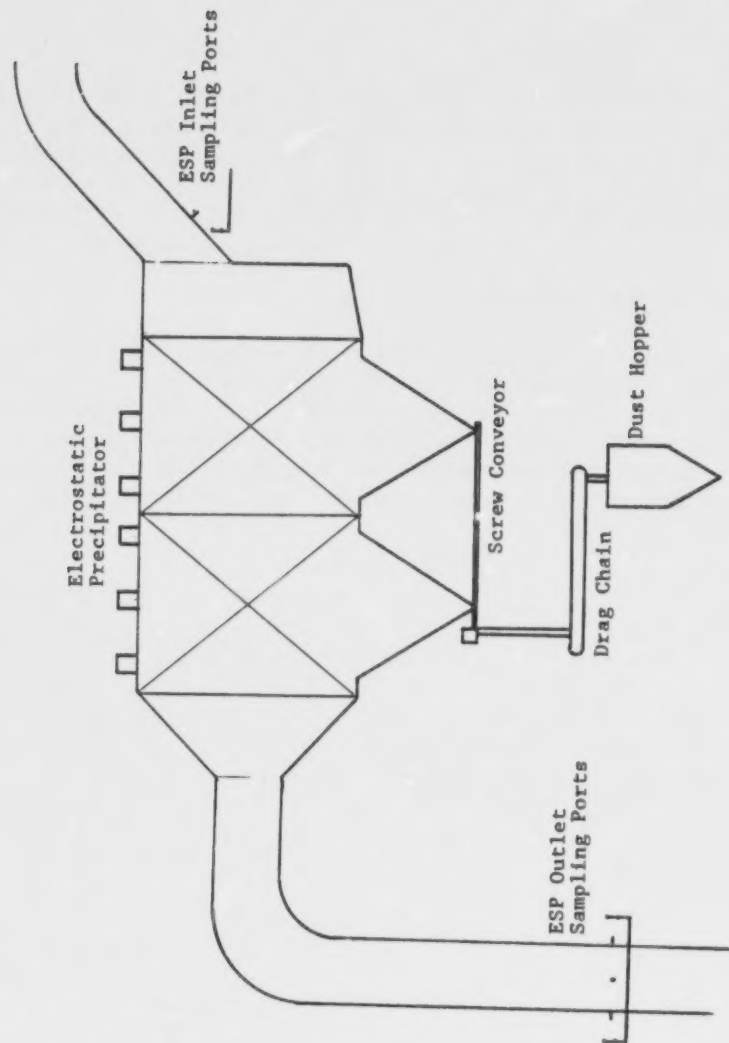


Figure 2-6. Electrostatic Precipitator and Dust Handling System.

SECTION 3

SAMPLING TECHNIQUES

Special sampling trains had to be built to meet the objectives set forward in the introduction. This section is intended to give a succinct survey of what sampling techniques were used. The equipment is described in greater detail in Volume II. The descriptions of the following sampling techniques are presented below:

- Wet Electrostatic Precipitator (WEP)
- Integral WEP Sampling Train
- Vapor Sampling Train
- Arsenic Sampling Train
- In/Out Stack Grain Loading Train
- Cyclone Sampling Train

All sampling was done isokinetically. Strict adherence to the EPA procedures as set forward in Method 1 was not possible at the ESP inlet due to the duct configuration and the location of the sampling ports. Sampling at the outlet was more ideal. Bends in the duct occurred approximately 4.5 stack diameters upstream and two stack diameters downstream of the sampling port location. In addition, the duct ran vertically thus avoiding stratification of particulate matter. The duct configuration at the inlet and outlet of the hot electrostatic precipitator as well as the traversing steps are described in detail in Volume II.

WET ELECTROSTATIC PRECIPITATOR

The wet electrostatic precipitator (WEP) used to collect particulates and acid mist is described first. It is part of the Integral WEP Sampling Train designed to collect solids, mist and gaseous components from a gas stream and is shown in Figure 3-1. An electrolyte is circulated through a round bottom flask and a vertical glass cylinder by a peristaltic pump. The walls of the cylinder are wetted by the falling film of electrolyte. A thin platinum wire is suspended in the center of the glass cylinder. A high voltage of 12-15 KV-DC causes a corona discharge at the center electrode.

The gas entering the WEP is first scrubbed and cooled in the round bottom flask. Particulates and mist not retained here are electrically charged in the glass cylinder, collected in the falling film and washed into the electrolyte reservoir. This sampling device does not clog like a filter or a thimble and no analytical background corrections are necessary since no extraneous material is introduced as is the case with filters.

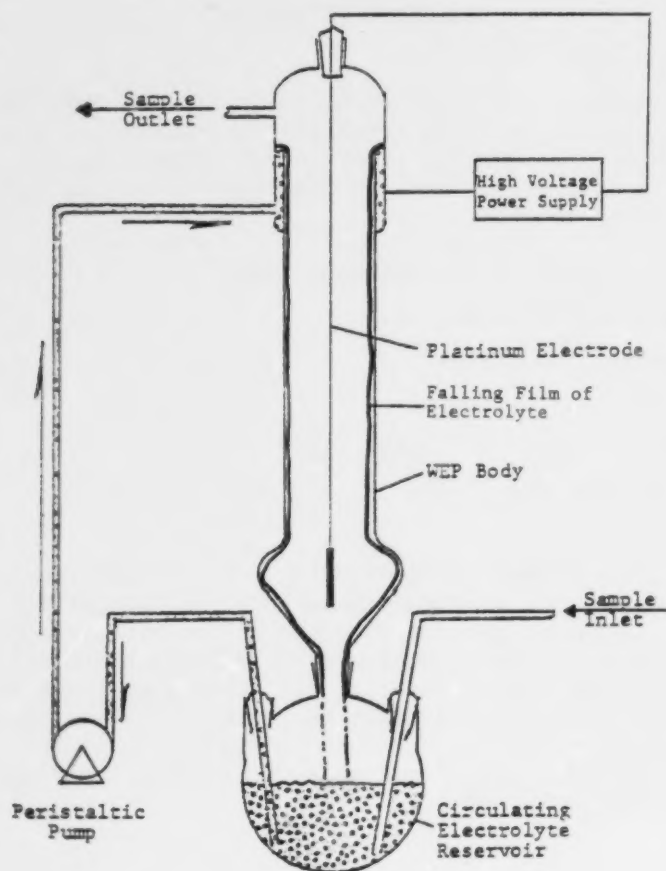


Figure 3-1. Wet Electrostatic Precipitator.

INTEGRAL WEP SAMPLING TRAIN

The wet electrostatic precipitator was integrated into the sampling device shown in Figure 3-2. The probe consisted of a pyrex nozzle and was pyrex lined. Teflon tubing was used to connect it with the WEP. All the lines were rinsed after sampling. The WEP was followed with eight impingers in an ice bath. The charge of the impingers is summarized in Table 3-1. A pump and a dry gas meter completed the assembly. Samples were collected on

July 11, 1976 at the inlet and outlet duct of the electrostatic precipitator. The samples were used to establish an element balance around the ESP.

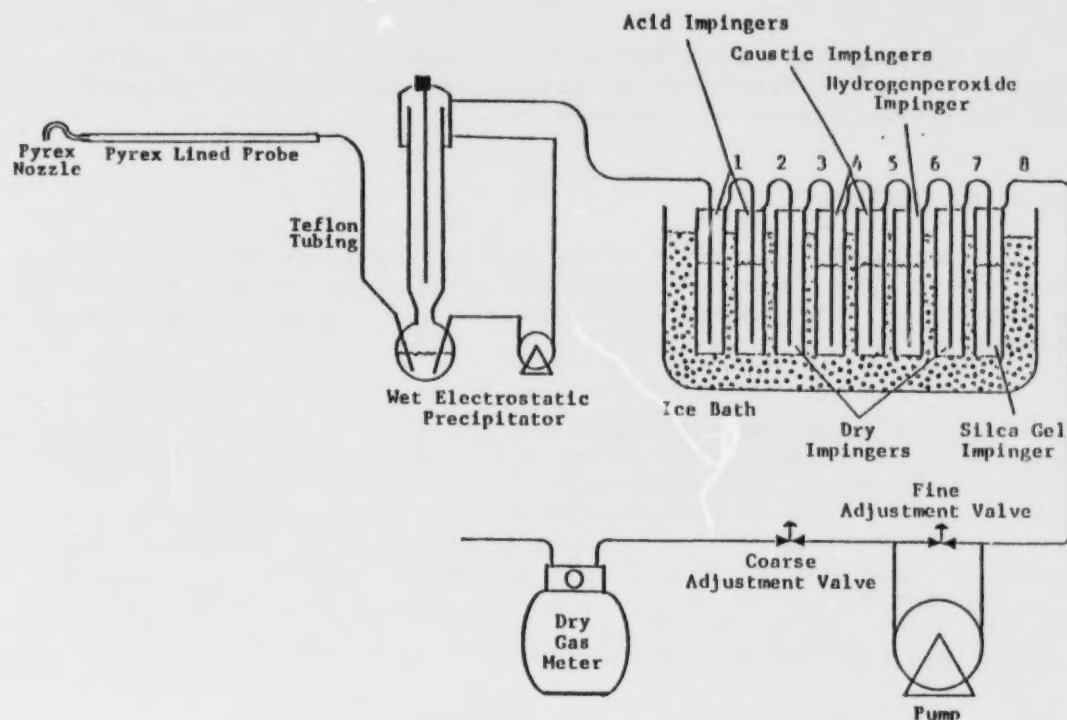


Figure 3-2. Schematic of the Integral WEP Sampling Train.

TABLE 3-1. IMPINGER SOLUTIONS USED FOR ESP MATERIAL BALANCE

Impinger Number	Solutions
1, 2	1:1:1 sulfuric acid, nitric acid, deionized water in a Smith-Greenburg impinger
3, 7	dry modified Smith-Greenburg impingers
4, 5	20% potassium hydroxide in a Smith-Greenburg impinger
6	hydrogen peroxide in a Smith-Greenburg impinger
8	preweighed silica gel in a modified Smith-Greenburg impinger

An additional sample was collected on July 13, 1977 with this train. This sample was used to study the element balance around the reverberatory furnace.

The sampling train shown in Figure 3-2 collects an integral sample consisting of particulates, mist and gaseous species which are collected in the WEP electrolyte and the impinger train.

VAPOR PHASE SAMPLING TRAIN

The temperature of matte and slag in a reverberatory furnace ranges typically from 1950-2300°F. Certain chemical compounds are vaporized at this temperature. The temperature of the flue gas is lowered to 600°F in waste heat boilers.

A vapor train as shown in Figure 3-3 was built to determine which compounds are still in the flue gas as vapors at this temperature. This train was used at the outlet of the electrostatic precipitator on July 16, 1977 to collect a vapor sample. A pyrex nozzle was attached to a pyrex-lined, heat traced probe. The probe was connected to an out-of-stack oven kept at duct temperature. The oven housed a cyclone followed by a filter. The impinger train following the out-of-stack oven was the same as that used for the integral WEP train. The cyclone-filter arrangement retained particulates. The impinger train collected species condensable between 600°F and 32°F.

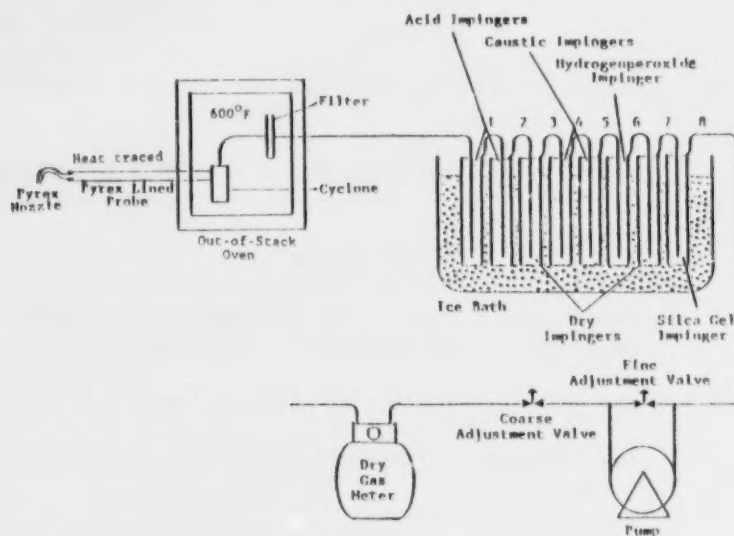
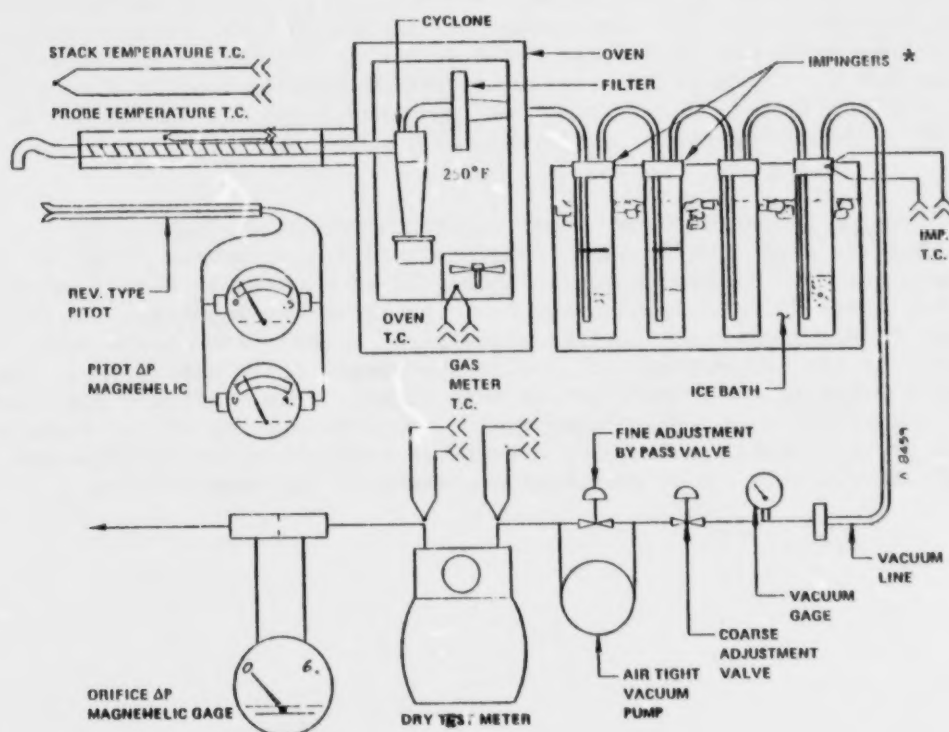


Figure 3-3. Schematic of the Vapor-Phase Trace Element Sampling Train.

ARSENIC SAMPLING TRAIN

The arsenic sampling train shown in Figure 3-4 was used to collect three integral arsenic samples each at the inlet and outlet. The inlet samples were obtained on July 13 (0930-1225) and July 14 (0555-0907; 1132-1505). Corresponding times for the outlet samples were July 13 (0951-1336) and July 14 (0610-0855; 1130-1415).

The content of the impinger solutions are described in Table 3-2. Two sampling ports each at the inlet west duct and inlet east duct were traversed. Strict adherence to EPA Method 1 was followed for sampling at the outlet. This duct was traversed from the north and west port. A total of 18 points on each traverse was covered. Wall condensation caused by cooling the gas from 600°F to 250°F was observed. The deposit having a reddish appearance could not be completely removed causing the analytical results to be potentially low. The samples collected with this device were analyzed by Battelle, Columbus Laboratories, Columbus, Ohio.



*Actually six impingers.

Figure 3-4. Arsenic Sampling Train (Modified EPA-5 Train).

TABLE 3-2. IMPINGER SOLUTIONS USED FOR ARSENIC SAMPLING

Impinger Number	Content	Impinger Number	Content
1	10% H ₂ O ₂ (250 ml)	4	.1 N NaOH (250 ml)
2	10% H ₂ O ₂ (250 ml)	5	.1 N NaOH (250 ml)
3	10% H ₂ O ₂ (250 ml)	6	Silica Gel

Arsenic sampling at the ESP outlet was repeated by plant personnel during the period of March 1, 1977 through March 3, 1977. The sampling procedure they used incorporated a combination of the EPA Methods 5 (particulate determination) and Method 8 (sulfuric acid mist and SO₂). Additionally, the method was designed to collect arsenic or arsenic compounds on the particulate filter, in the first two impingers (each containing 200 ml 1% HNO₃) and on the inline (or Method 8) filter.

A major deviation from normal testing occurred during the ESP outlet tests conducted by plant personnel. A full traverse could not be accomplished. This deviation was caused by an abnormally high loading on the inline filter located down stream from the first two impingers. A yellow-orange to orange-red particulate material of a very fine nature would collect on this filter and subsequently raise the sample train vacuum until the isokinetic sampling rate could not be maintained. This condition would develop in a very short time and, consequently, the sample sizes of the tests are below the acceptable amount for a reliable test. A major modification of the sampling equipment would have been necessary to continue testing.

IN-STACK (600°F)/OUT-OF-STACK (250°F) GRAIN LOADINGS

The gas temperature at the ESP outlet is approximately 600°F. Certain compounds, especially sulfuric acid mist condense if the gas is cooled to 250°F as is recommended in EPA Method 5. The increase in grain loading determination caused by condensation was determined using the in-stack/out-of-stack sampling train shown in Figure 3-5. The equipment is the same as that shown in Figure 3-4 with the exception that a filter was inserted into the duct to collect the material solid at duct temperature. Three determinations were made on July 15, 1977.

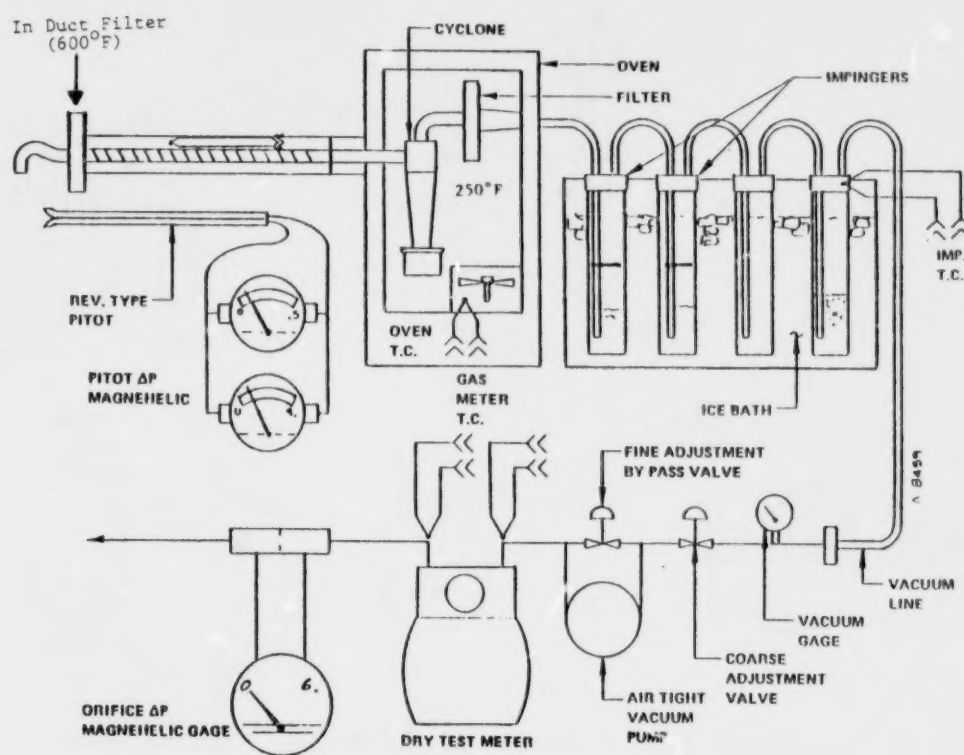


Figure 3-5. In-Stack/Out-of-Stack Sampling Train.

CYCLONE SAMPLING TRAIN

The train shown in Figure 3-6 was constructed to separate the particulate matter into three size fractions using cyclones. A difference in the chemical composition of each fraction would have indicated that an evaporation condensation mechanism and/or a selective removal of particles as a function of composition occurs in the ESP.

The oven was kept at duct temperature. However, a separation was unsuccessful due to the sticky nature of the deposit in the cyclones.

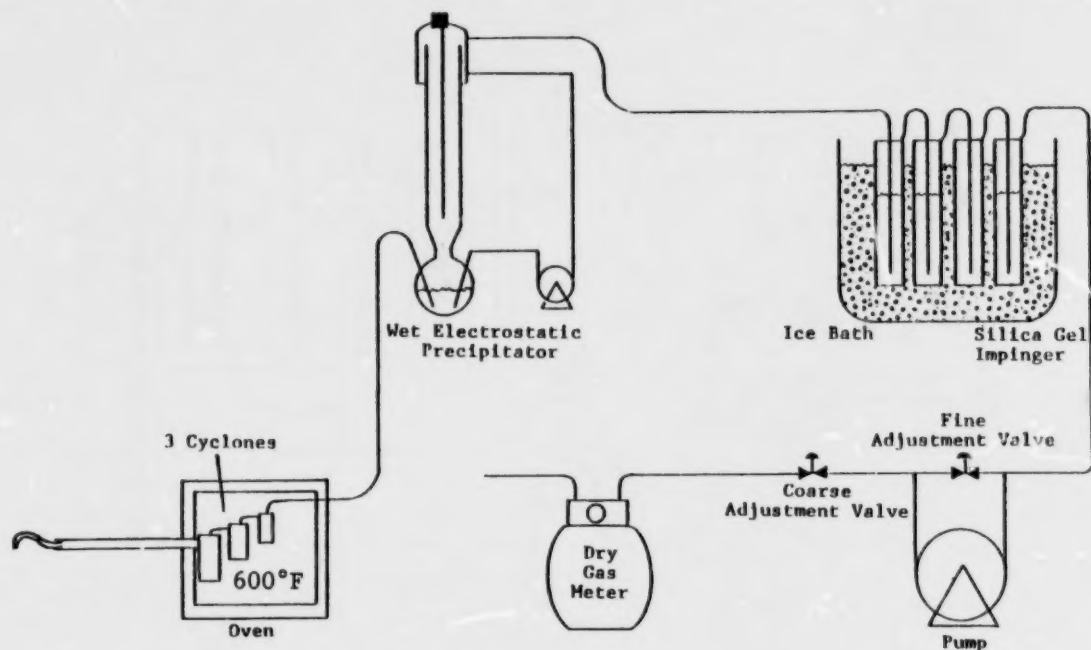


Figure 3-6. Schematic of the Cyclone Sampling Train.

SECTION 4

RESULTS AND DISCUSSION OF RESULTS

The results are presented in such a manner as to follow the flow of the material through the smelter. The compositions of concentrate, matte and slag are discussed first. The reverberatory furnace element balance is discussed next. A complete material balance around the reverberatory furnace could not be established due to the lack of samples from several streams. Some general conclusions, however, are drawn.

Two sections discussing experimental results of arsenic sampling follow. Data taken by smelter personnel are presented first. Data generated by Radian are presented in the following section. Discussions of the electrostatic precipitator efficiency, the electrostatic precipitator material balance, and the major crystalline species present at the smelter conclude the section.

REVERBERATORY FURNACE FEED

A composite of the concentrate feed to the reverberatory furnace was collected during July 12, 1976 through July 14, 1976 by emptying the slinger bin catches at the end of each shift. Measurements of the converter slag and recycle dusts fed to the reverb were not possible. The measured concentration of an element was multiplied by the flow rate of the concentrate. The average element flows obtained in this manner for the July 12 through July 14, 1976 period are shown in Table 4-1.

TABLE 4-1. ELEMENT CONCENTRATION AND FLOWS IN THE REVERBERATORY FURNACE FEED

Element	Analysis Technique	Concentration in Feed (ppm)	Flow Rate (lb/hr) Calculated
Arsenic	AA	3900	190
Cadmium	AA	1200	59
Molybdenum	AA	1600	79
Lead	AA	980	49
Antimony	AA	120	6
Selenium	F	200	10
Zinc	AA	830	42
Fluorine	SIE	67	3

AA - atomic absorption spectrophotometry

F - fluorometric determination

SIE - specific ion electrode using the method of standard additions

The concentrate was also analyzed by semiquantitative spark source mass spectrometry (SSMS) analysis. This technique shows a detection limit of 0.1 to 1 ppm for solids. Elements present in a concentration higher than 1000 ppm are listed as major components (MC). The results are summarized in Table 4-2. Species entering as major components (>1000 ppm) are:

Arsenic	Calcium	Aluminum
Copper	Potassium	Magnesium
Iron	Sulfur	Sodium
Titanium	Silicon	

Species showing a concentration in the order of 50-1000 ppm are:

Bismuth	Antimony	Zinc
Lead	Molybdenum	Nickel
Barium	Selenium	Fluorine

The rest of the 71 elements surveyed show concentrations in the low ppm range or are not detectable.

The high arsenic concentration in the concentrate is noteworthy. Data measured by plant personnel during February 28, 1977 through March 4, 1977 are summarized in Table 4-3. They show values in the same order of magnitude. The fluctuations from day to day and even from shift to shift, however, are significant. The maximum concentration was 7360 ppm during the B shift on March 1, 1977, the minimum was 780 ppm during the B shift on March 4, 1977. The feed concentration of arsenic varies widely. Therefore, sampling must be time phased to permit meaningful comparison of measurements. Material balances can only be completed using time phased measurements.

α -Quartz and chalcopyrites, CuFeS_2 , were found to dominate the X-ray diffraction pattern taken from the concentrate.

TABLE 4-2. SURVEY ANALYSIS OF THE REVERBERATORY FURNACE FEED BY SSMS
(SAMPLES COLLECTED JULY 12, 1976 THROUGH JULY 14, 1976)

CONCENTRATION IN PPM WEIGHT							
ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	2	Terbium	0.4	Ruthenium		Vanadium	11
Thorium	4	Gadolinium	1	Molybdenum	340	Titanium	MC
Bismuth	80	Europium	0.6	Niobium	3	Scandium	3
Lead	910	Samarium	3	Zirconium	*32	Calcium	MC
Thallium	≤1	Neodymium	6	Yttrium	5	Potassium	MC
Mercury	NR	Praseodymium	3	Strontium	36	Chlorine	25
Gold	0.7	Cerium	17	Rubidium	19	Sulfur	MC
Platinum		Lanthanum	10	Bromine	5	Phosphorus	15
Iridium		Barium	320	Selenium	110	Silicon	MC
Osmium		Cesium	0.7	Arsenic	MC	Aluminum	>250
Rhenium	0.5	Iodine	1	Germanium	2	Magnesium	MC
Tungsten	2	Tellurium	4	Gallium	6	Sodium	>600
Tantalum	≤0.6	Antimony	70	Zinc	330	Fluorine	≈160
Hafnium		Tin	9	Copper	MC	Oxygen	NR
Lutetium		Indium	STD	Nickel	190	Nitrogen	NR
Ytterbium		Cadmium	*16	Cobalt	17	Carbon	NR
Thulium		Silver	40	Iron	MC	Boron	2
Erbium	0.4	Palladium		Manganese	25	Beryllium	<0.1
Holmium	0.7	Rhodium		Chromium	10	Lithium	1
Dysprosium	1					Hydrogen	NR

NR - SSMS technique is not suitable.

No value listed: Element concentration is below the detection limit of
SSMS (0.1-1 ppm for solids, 1-10 ppb for liquids)

MC - Major component, read out is off the scale on SSMS.

* - Sample not homogenous with respect to these elements

TABLE 4-3. VARIATION OF ARSENIC CONCENTRATION IN REVERBERATORY FURNACE FEED (DATA BY SMELTER PERSONNEL)

Sample	% Arsenic
A Shift 2/28/77	0.132 .148 Average = 0.140
B Shift 2/28/77	0.120 .120 Average = 0.120
C Shift 2/28/77	0.290 .290 Average = 0.290
A Shift 3/1/77	0.384 .352 Average = 0.369
B Shift 3/1/77	0.713 .714 .749 .769 Average = 0.736
C Shift 3/1/77	0.310 .300 Average = 0.305
A Shift 3/2/77	0.134 .125 .148 .156 Average = 0.141
B Shift 3/2/77	0.240 .240 Average = 0.240
C Shift 3/2/77	0.320 .348 Average = 0.334
A shift 3/3/77	0.306 .300 .306 .306 Average = 0.305
B Shift 3/3/77	0.235 .220 Average = 0.228
C Shift 3/3/77	0.401 .400 Average = 0.401
A Shift 3/4/77	0.185 .175 Average = 0.180
B Shift 3/4/77	0.080 .075 Average = 0.078
C Shift 3/4/77	0.369 .373 Average = 0.371

REVERBERATORY FURNACE SLAG

The concentration and flows of the elements found in high concentration in the feed are listed in Table 4-4 for the reverberatory furnace slag. These results are extremely interesting. They indicate that the slag contains 25 percent of the arsenic, 27 percent of the lead and only a trace of the cadmium which enters the reverberatory furnace. Only half of the incoming antimony and selenium leave the smelter in this stream. Two-thirds of the fluorine and zinc are discharged with the slag, while molybdenum is almost completely contained in the slag.

Elements depleted in the slag must be present in other smelter exit streams.

TABLE 4-4. REVERBERATORY FURNACE SLAG COMPOSITION AND ELEMENT FLOW RATES (JULY 12-14, 1976)

Element	Analysis Technique	Concentration in Slag (ppm)	Flow Rate (lb/hr) Calculated
Arsenic	AA	1300	48
Cadmium	AA	9	.3
Molybdenum	AA	2400	89
Lead	AA	350	13
Antimony	AA	92	3
Selenium	F	150	5
Zinc	AA	810	30
Fluorine	SIE	55	2

AA - atomic absorption spectrophotometry

F - fluorometric determination

SIE - specific ion electrode using the method of standard additions

The survey analysis of the reverberatory furnace slag by SSMS is shown in Table 4-5. Major components (>1000 ppm) are the following:

Molybdenum	Titanium	Silicon
Arsenic	Calcium	Aluminum
Zinc	Potassium	Magnesium
Copper	Sulfur	Sodium
Iron	Phosphorus	

TABLE 4-5. SURVEY ANALYSIS OF REVERBERATORY FURNACE SLAG
BY SSMS (SAMPLES COLLECTED JULY 12, 1976 THROUGH
JULY 14, 1976)

CONCENTRATION IN PPM WEIGHT							
ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	9	Terbium	0.5	Ruthenium		Vanadium	15
Thorium	24	Gadolinium	3	Molybdenum	MC	Titanium	MC
Bismuth	5	Europium	1	Niobium	10	Scandium	4
Lead	370	Samarium	10	Zirconium	130	Calcium	MC
Thallium		Neodymium	12	Yttrium	18	Potassium	MC
Mercury	NR	Praseodymium	10	Strontium	130	Chlorine	95
Gold		Cerium	65	Rubidium	44	Sulfur	MC
Platinum		Lanthanum	50	Bromine	2	Phosphorus	MC
Iridium		Barium	270	Selenium	25	Silicon	MC
Osmium		Cesium	4	Arsenic	MC	Aluminum	>250
Rhenium		Iodine		Germanium	0.6	Magnesium	MC
Tungsten	4	Tellurium		Gallium	8	Sodium	>640
Tantalum		Antimony	160	Zinc	MC	Fluorine	≈60
Hafnium	3	Tin	15	Copper	MC	Oxygen	NR
Lutetium	0.3	Indium	STD	Nickel	14	Nitrogen	NR
Ytterbium	1	Cadmium	4	Cobalt	38	Carbon	NR
Thulium	0.3	Silver	1	Iron	MC	Boron	2
Erbium	1	Palladium		Manganese	260	Beryllium	0.2
Holmium	1	Rhodium		Chromium	120	Lithium	2
Dysprosium	5					Hydrogen	NR

NR - SSMS technique is not suitable.

No value listed: Element concentration is below the detection limit of
SSMS (0.1-1 ppm for solids, 1-10 ppb for liquids)

MC - Major component, read out is off the scale on SSMS.

Species showing a concentration in the order of 50-1000 ppm are:

Lead	Strontium
Barium	Manganese
Antimony	Chromium
Zirconium	Fluorine

The concentration of arsenic in the slag is shown in Table 4-6. These data were measured by plant personnel during the period of March 1, 1977 through March 4, 1977. The arsenic concentration in the reverberatory slag of 700-800 ppm reported by smelter personnel compares to 1300 ppm found during the July 12 through July 14, 1976 period.

TABLE 4-6. ARSENIC CONCENTRATION IN THE REVERBERATORY SLAG
DURING MARCH 1, 1977 THROUGH MARCH 3, 1977
(DATA BY SMELTER PERSONNEL)

Sample	% Arsenic
B Shift 3/1/77	0.065 .065 Average = 0.065
A Shift 3/2/77	0.083 .093 Average = 0.088
A Shift 3/3/77	0.066 .076 Average = 0.071
B Shift 3/3/77	0.085 .086 Average = 0.086

It is noteworthy that the fluctuations are small if compared to those observed in the concentrate (see Table 4-3). The melt in the reverberatory furnace evidently acts as damper. The residence time is in the order of 12 to 20 hours. Fluctuations in the feed concentration can therefore be expected to be smoothed in the matte and reverberatory furnace slag. This is, however, not true for volatile compounds like As_2O_3 , which can be expected to leave the furnace immediately upon formation due to the high vapor pressure at furnace temperature.

REVERBERATORY FURNACE MATTE

The concentrations and flow rates of the same species in the matte are listed in Table 4-7.

TABLE 4-7. CONCENTRATION OF SELECTED ELEMENTS IN MATTE (COMPOSITE SAMPLE JULY 12 THROUGH JULY 14, 1976)

Element	Analysis Technique	Concentration in Matte (ppm)	Flow Rate (lb/hr) Calculated
Arsenic	AA	1100	48
Cadmium	AA	880	37
Molybdenum	AA	200	8
Lead	AA	2000	84
Antimony	AA	110	5
Selenium	F	4	.2
Zinc	AA	750	31
Fluorine	SIE	<.3	<.01

This data indicate that only minor amounts of the incoming molybdenum, selenium and fluorine are contained in the matte. This combined with the results of the reverberatory slag analysis indicates that major parts of the elements:

- arsenic,
- selenium, and
- fluorine,

leave the reverberatory furnace with the reverberatory furnace off-gases.

Molybdenum is primarily retained in the reverb and discharged with the slag.

The major amounts of cadmium, lead and zinc are transported with the matte to the converters.

The semiquantitative results of the SSMS analysis are given in Table 4-8. Again, the samples are composites for the days July 12 through July 14, 1976.

TABLE 4-8. SURVEY ANALYSIS OF MATTE BY SPARK SOURCE MASS SPECTROMETRY (COMPOSITE SAMPLE FOR JULY 12 THROUGH JULY 14, 1976)

CONCENTRATION IN PPM WEIGHT							
ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	≤3	Terbium		Ruthenium		Vanadium	1
Thorium	≤3	Gadolinium		Molybdenum	170	Titanium	26
Bismuth	120	Europium		Niobium		Scandium	≤0.4
Lead	MC	Samarium		Zirconium	5	Calcium	MC
Thallium	3	Neodymium		Yttrium	2	Potassium	MC
Mercury	NR	Praseodymium	0.4	Strontium	14	Chlorine	19
Gold	3	Cerium	0.7	Rubidium	3	Sulfur	MC
Platinum		Lanthanum	0.9	Bromine	1	Phosphorus	6
Iridium		Barium	36	Selenium	410	Silicon	470
Osmium		Cesium	0.2	Arsenic	MC	Aluminum	>350
Rhenium		Iodine		Germanium		Magnesium	15
Tungsten		Tellurium	6	Gallium	0.2	Sodium	MC
Tantalum		Antimony	180	Zinc	MC	Fluorine	≈25
Hafnium		Tin	30	Copper	MC	Oxygen	NR
Lutetium		Indium	STD	Nickel	60	Nitrogen	NR
Ytterbium		Cadmium	50	Cobalt	570	Carbon	NR
Thulium		Silver	110	Iron	MC	Boron	0.4
Erbium		Palladium		Manganese	34	Beryllium	
Holmium		Rhodium		Chromium	15	Lithium	1
Dysprosium						Hydrogen	NR

NR - SSMS technique is not suitable.

No value listed: Element concentration is below the detection limit of SSMS (0.1-1 ppm for solids, 1-10 ppb for liquids)

MC - Major component.

Species found in major concentrations (>1000 ppm) are:

Lead	Copper	Potassium
Arsenic	Iron	Sulfur
Zinc	Calcium	Sodium

Elements found in the concentration in the order of 100-1000 ppm are:

Bismuth	Molybdenum	Cobalt
Antimony	Selenium	Silicon
Cadmium	Nickel	Aluminum
Silver		

The rest of the 71 elements surveyed show concentrations below the detection limit or are present in the low ppm range.

The fluctuation of the matte arsenic concentration was measured by smelter personnel during the period March 1 through March 3, 1977. The average concentration found for the three days was approximately 900 ppm (see Table 4-9). The fluctuations observed in the concentrate are dampened as was observed for the slag. Again, the residence time of the melt in the reverberatory furnace of approximately 12-20 hours being the reason. The average value of 900 ppm for the March 1977 period compares to 1100 ppm determined for the July 12 through July 14, 1976 period determined by Radian.

TABLE 4-9. FLUCTUATION OF THE ARSENIC CONCENTRATION IN THE MATTE FOR THE PERIOD MARCH 1 THROUGH MARCH 3, 1977 (DATA DETERMINED BY SMELTER PERSONNEL)

Sample	Sample No.	% Arsenic
B Shift 3/1/77	497	0.079 .093 Average = 0.086
A Shift 3/2/77	505	0.102 .108 Average = 0.105
A Shift 3/3/77	501	0.080 .032 Average = 0.081
B Shift 3/3/77		0.092 .120 .100 Average = 0.104

REVERBERATORY FURNACE ELEMENT BALANCE (JULY 12-14, 1976)

The original sampling plan was designed to encompass the electrostatic precipitator servicing the reverberatory furnace only, but plant personnel made concentrate, reverberatory furnace slag and matte samples available for analysis during the July sampling effort. Flow rates around the reverb were released to Radian in February 1977. The values are given in Volume II.

A rigorous material balance around the reverberatory furnace is still not possible due to the lack of the following samples:

- converter slag,
- converter dust, and
- reverberatory furnace waste heat boiler dust.

Certain conclusions concerning the fate of the elements entering the plant as minor components with the feed are still possible.

Arsenic, cadmium, molybdenum, antimony, selenium, zinc and fluorine were the trace elements appearing in the highest concentration. The concentration of these elements in the matte, reverberatory slag and gas streams indicate their pathway through the smelter.

Molybdenum

It is evident from Table 4-10 that nearly all the molybdenum is trapped in the reverb slag and discharged with this stream. Reverb ESP dust and matte contain only a minor percentage of the molybdenum entering the furnace.

Arsenic

From the 190 lb/hr of arsenic entering the furnace roughly 1/4 is transported with the matte to the converters and roughly 1/4 is discharged with the slag. About 1/2 leaves the reverberatory furnace with the flue gas. The majority of this amount is not retained by the electrostatic precipitator.

Arsenic values measured by plant personnel in the electrostatic precipitator dust, the waste heat boiler dust, the converter dust and the acid plant purge water during the March 1977 sampling effort are summarized in Table 4-11. The low values of 1.7 percent of As in the converter dust and 0.013 percent in the acid plant purge water are consistent with the observations made by Radian during the July 1976 sampling effort.

TABLE 4-10. ELEMENT FLOW RATES IN THE FEED AND DISCHARGE STREAMS OF THE REVERBERATORY FURNACE (lbs/hr) (RADIAN DATA)

Element	Incoming Streams			Total	Outgoing Streams					Waste Heat* Boiler Dust	Total
	Reverb Feed	Converter Slag	Converter Dust		Matte	Slag	Flue Outlet	ESP* Catch			
Al	400			>400	<17	700	0.10	1.1			~700
As	190			>190	48	48	76	30			~200
Ba	31			>31	33	43	0.64	0.023			~76.2
Be	0.072			>0.072	4.1x10 ⁻³	0.032	3.4x10 ⁻³	4.0x10 ⁻⁶			~0.039
Ca	770			>770	12	1.9x10 ³	0.011	2.1			~2000
Cd	59			>59	37	0.33	.076	0.74			~46
Cr	0.076			>0.076	0.64	3.8	0.044	0.018			~4.5
Cu	1.6x10 ⁶			>1.6x10 ⁶	1.8x10 ⁶	2.2x10 ²	1.8	62			~1.8x10 ⁶
F	3.4			>3.4	0.012	2.2	9.4	0.032			~12
Fe	1.0x10 ⁶			>1.0x10 ⁶	1.1x10 ⁶	1.2x10 ⁶	0.55	42.6			~2.3x10 ⁶
Hg	0.018			>0.018	0.020	9.1x10 ⁻³	0.033	1.5x10 ⁻⁶			~0.062
Mo	79			>79	8.5	89	0.17	6.6			~100
Ni	0.70			>0.70	2.0	0.76	0.011	0.059			~29
Pb	49			>49	84	13	0.38	5.3			~100
Sb	6.0			>6.0	4.6	3.4	0.030	1.3			~9.4
Se	10			>10	0.17	5.5	0.65	0.16			~6.5
Si	1100			>1100	<42	4.8x10 ³	1.7	1.7			~4800
V	0.92			>0.92	0.33	0.86	0.027	0.011			~1.2
Zn	42			>42	31	30	0.22	4.6			~66

* These streams were not recycled during the time of ESP sampling.

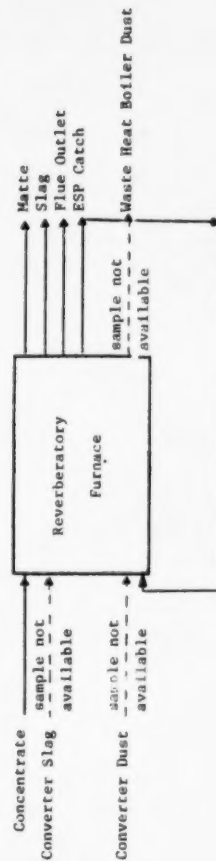


TABLE 4-11. ARSENIC CONCENTRATION IN THE WASTE HEAT BOILER DUST, REVERB ESP DUST, CONVERTER DUST AND ACID PLANT PURGE WATER (DATA BY PLANT PERSONNEL)

Date	Sample	% Arsenic
3/1/77	Reverb ESP Dust	5.5 5.6 5.7 Average = 5.6
3/2/77	Reverb ESP Dust	5.0 5.1 Average = 5.1
3/3/77	Reverb Dust	4.1 4.9 Average = 4.5
3/4/77	Reverb ESP Dust	5.3 5.0 Average = 5.2
3/5/77	Reverb ESP Dust	4.5 4.8 Average = 4.7
3/6/77	Reverb ESP Dust	3.3 3.5 Average = 3.4
3/7/77	Reverb ESP Dust	3.3
3/1/77	Waste Heat Boiler Dust (Reverb)	6.5 6.5 Average = 6.5
3/2/77	Waste Heat Boiler Dust (Reverb)	4.7 4.6 Average = 4.7
3/1/77	Converter Dust	1.8 1.9 Average = 1.9
3/2/77	Converter Dust	1.3 1.4 Average = 1.4
4/3/77	Acid Plant Purge Water	0.0013 .0012 .0014 Average = 0.0013

Selenium

The selenium data are not quite conclusive. Fifty percent of the incoming selenium is discharged with the slag. The flows found in the matte, flue outlet and ESP catch do not account for the rest. A potential explanation could be condensation of a volatile selenium compound in the reverberatory waste heat boilers.

The phase of the selenium compound escaping the reverb ESP could not be identified. The X-ray diffraction pattern did not match the lines of elemental selenium, known selenium oxides, or selenium sulfide.

ARSENIC MATERIAL BALANCE AROUND THE SMELTER (SMELTER DATA)

An arsenic material balance around the smelter was established by plant personnel. Inputs to this balance were composite samples and flows for the whole month of January. The analytical values used in this balance are shown in Table 4-12 with exception of the acid plant purge water. That part of the smelter included in the balance is shown in Figure 4-1.

TABLE 4-12. ARSENIC CONCENTRATIONS IN INCOMING AND OUTGOING STREAMS OF THE REVERBERATORY FURNACE DURING THE MONTH OF JANUARY 1977
(DATA BY PLANT PERSONNEL)

Sample	% Arsenic
Smelter Concentrate	0.280
Composite, Jan. 1977	.270
	.250
	.248
	Average = 0.262
Matte Composite	0.074
Jan. 1977	.080
	Average = 0.077
Reverberatory Slag	0.061
Composite, Jan. 1977	.064
	Average = 0.063
Reverberatory Precipitator	4.4
Dust Composite, Jan. 1977	4.4
	Average = 4.4
Converter Precipitator	7.7
Dust Composite, Jan. 1977	
Converter Flue Dust	1.7
Composite, Jan. 1977	1.8
	Average = 1.8
Converter Slag	0.014
Composite, Jan. 1977	.015
	Average = 0.015
Anode Copper	0.029
Composite, Jan. 1977	0.029
	Average = 0.029

The following flows were found based on plant data:

Incoming Streams: (Average for January 1977)

Point ①: Concentrate Feed	101.9 lb/hr
Point ②: Lime Rock Feed	<u>0.0 lb/hr</u>
TOTAL ARSENIC IN:	101.9 lb/hr

Outgoing Streams: (Average for January 1977)

Point ③: Reverb Furnace Slag	25.7 lb/hr
Point ④: Acid Plant Purge Water	27 lb/hr
Point ⑤: Anode Copper	4.6 lb/hr
Point ⑥: Reverb ESP Outlet	<u>X</u>
TOTAL ARSENIC OUT	57.3 + X lb/hr

Reverb ESP Outlet = $101.9 - 57.3 = 44.6$ lb/hr

The value of 27 lb/hr used in the balance for acid plant purge water was determined from a sample taken March 4, 1977. Streams not included in this scheme comprise the tail gas and the sulfuric acid from the acid plant. The arsenic flow in these streams, however, can be expected to be very much smaller than that in the purge water stream.

These data indicate that roughly 50% (44.6 lb/hr) of the incoming arsenic (101.9 lb/hr) leaves the smelter with the reverberatory furnace flue gas, 25% (25.7 lb/hr) are discharged with the reverberatory furnace slag and 25% (27 lb/hr) are transported with the matte to the converters and leave the converters with the off-gases.

The same 50-25-25 split was indicated in the reverberatory balance for arsenic based on the samples obtained during the July 1976 sampling effort (see Table 4-10). The only major difference is that the arsenic flow rates in the streams is roughly double that measured by plant personnel during January. The difference can be explained if it is attributed to the wide arsenic fluctuations as indicated in Table 4-3.

The same balance attempt was repeated by plant personnel during March 1977. Average flows were as follows:

Incoming Streams:

Point ①: Concentrate Feed	103 lb/hr
Point ②: Lime Rock Feed	<u>0 lb/hr</u>
TOTAL ARSENIC IN	103 lb/hr

Outgoing Streams:

Point ③: Reverb Furnace Slag	31.1 lb/hr
Point ④: Acid Plant Purge Water	27.1 lb/hr
Point ⑤: Anode Copper	5.2 lb/hr
Point ⑥: Reverb ESP Outlet	<u>X</u>
TOTAL ARSENIC OUT	63.4 + X lb/hr

By difference:

$$\text{Reverb ESP Outlet } X = 103 - 63.4 = 39.6 \text{ lb/hr}$$

The actual values obtained by direct measurements during March were: 25 lb/hr (March 1, 1977), 34 lb/hr (March 2, 1977), and 49 lb/hr (March 3, 1977). Of these emissions, 16, 17 and 23 lb/hr was in the form of gaseous arsenic on March 1, March 2 and March 3, 1977 respectively. Difficulties were encountered due to the deposit of a yellow-orange material clogging the filter.

ARSENIC FLOW AT ESP INLET AND OUTLET (RADIAN DATA)

The arsenic sampling train described in Section 3 was used by Radian to collect samples for arsenic analysis on July 13 (9:51 a.m.-13:36 a.m.) and July 14, 1976. Both the inlet and outlet ducts were traversed. The exact sampling times, traverse points used and the flows determined are summarized in Table 4-13. Figures 4-2 and 4-3 help as visual guides to locate the sampling points indicated in Table 4-13.

Arsenic flow rates of 59.3, 72.9 and 75.4 lbs/hr giving an average of 69.2 lbs/hr were found at the inlet. The corresponding values at the outlet were 53.7, 44.8 and 51.3 lbs/hr or an average of 49.9 lbs/hr.

These values are slightly higher than the flows determined by difference by Smelter personnel (44.6 lb/hr for January and 39.6 lbs/hr for March). Direct measurements by plant personnel for March 1, 2 and 3, 1977 determined flows of 25, 34 and 49 lbs/hr.

TABLE 4-13. SUMMARY OF ARSENIC EMISSION DATA FROM THE REVERBERATORY ELECTROSTATIC PRECIPITATOR (RADIAN DATA)

Run	Date	Time (min.)	INLET		Arsenic Flow Rate (lbs/hr)	Time (min.)	OUTLET		Arsenic Flow Rate (lbs/hr)
			Gas Flow Rate (acfm)	Sampling Points			Gas Flow Rate (acfm)	Sampling Points	
1	7-13-76	0930-1226	155200	4-6 E; 13-15 E 4-6 W; 13-15 W	59.3	0951-1336	170700	N 7-16 W 1-17	53.7
2	7-14-76	0555-0907	156000	4-6 E; 13-15 E 4-6 W; 13-15 W	72.9	0610-0855	168900	N 1-17 W 1-17	44.8
3	7-14-76	1132-1505	157900	4-6 E; 13-15 E 4-6 W; 13-15 W	75.4	1130-1415	166500	N 1-17 W 1-17	51.3
Average	-	-	156400		69.2	-	168700		49.9

Other determinations by Radian showed a flow of 140 lb/hr (ESP balance on July 11) and 76 lb/hr (reverb balance July 13, 1976, 6:35 a.m.-10:28 a.m.). The 76 lb/hr are slightly more than the 53.7 lb/hr found with the arsenic train the same day only 4 hours later.

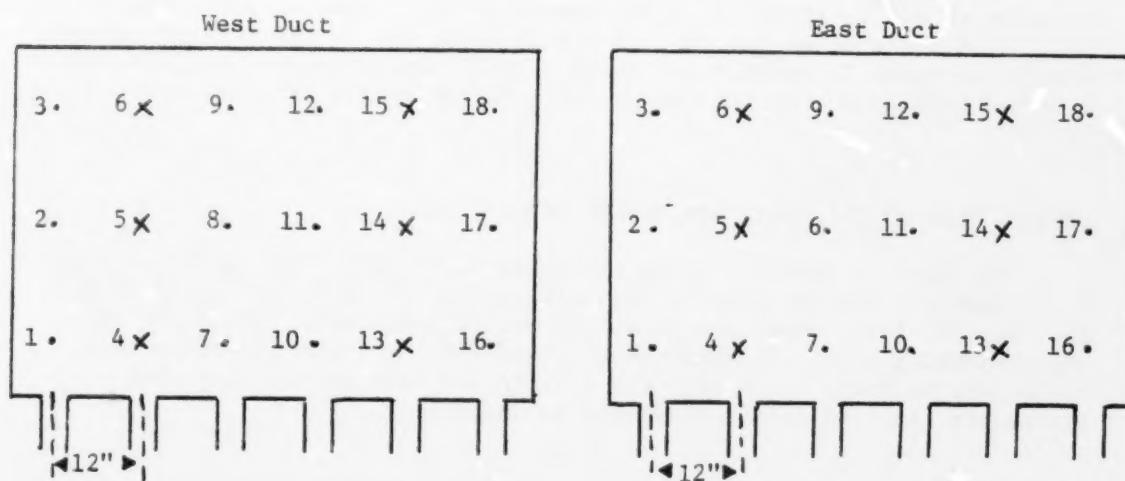


Figure 4-2. Traverse Points Layout for Reverberatory Electrostatic Precipitator Inlet.

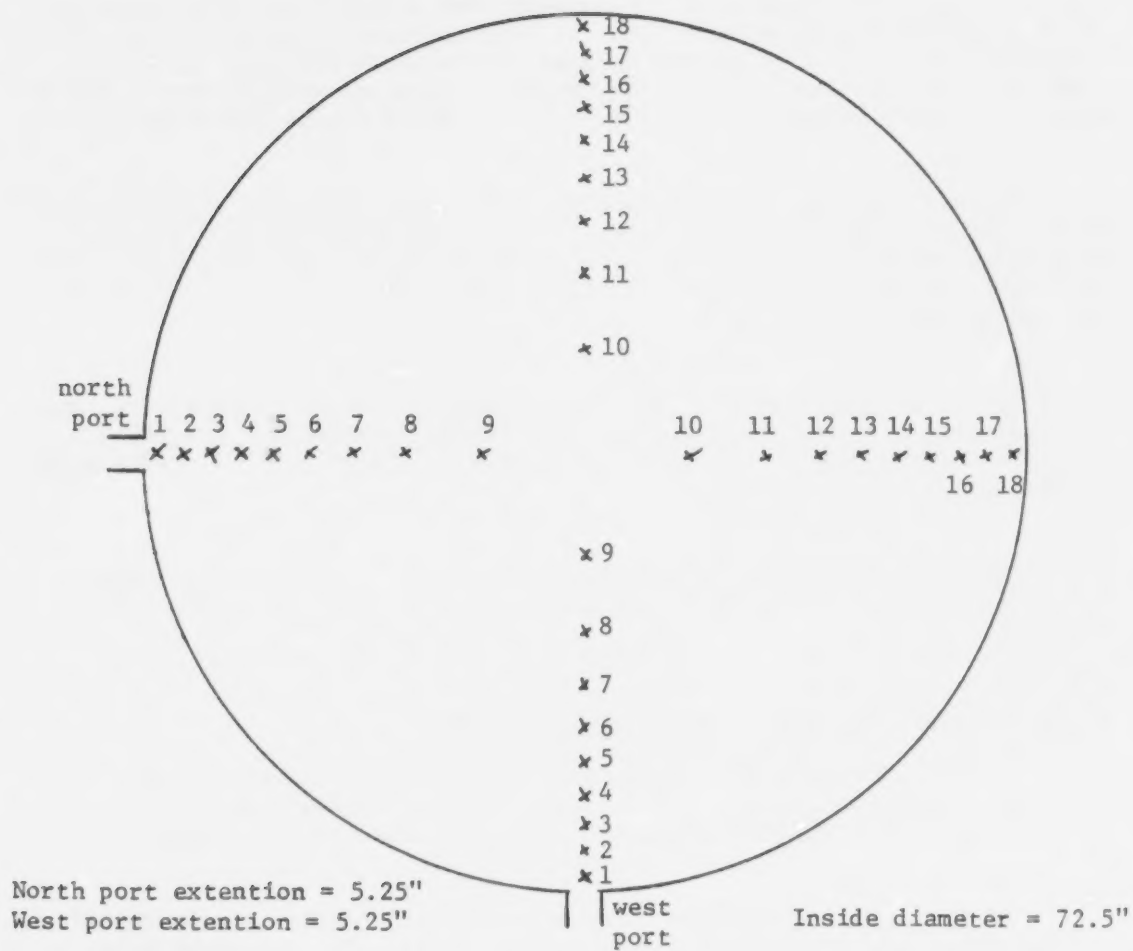


Figure 4-3. Traverse Points Layout for Reverberatory Electrostatic Precipitator Outlet.

COLLECTION EFFICIENCY OF THE ELECTROSTATIC PRECIPITATOR

In Stack Grain Loadings

The particulate sampling conditions at the inlet were quite nonideal due to the duct configuration. The problem was enhanced due to a surge in particulate concentration each time the reverberatory furnace was fed. In addition, the material collected clogged the in-stack sampling devices. Sampling with thimbles had to be abandoned in favor of in-duct Gelman filters. Duct temperature ranged typically from 575 to 650°F during these experiments.

The six sampling ports of both the inlet east and inlet west duct were traversed during the times and dates indicated in Table 4-14. A schematic showing the sample point numbers is included in Table 4-14. The grain loadings varied from .358 grains/scf to 1.552 grains/scf and showed an average of 0.60 grains/scf.

The measurements at the ESP outlet showed much less fluctuation. The ESP evidently dampened the surge in grain loading observed at the inlet. Dates, times and duct locations are summarized in Table 4-15. Average grain loading was 0.020 grains/scf.

The overall particulate removal efficiency of the ESP was calculated to be 96.7% @ 600°F which is in excellent agreement with the design efficiency of 96.8%.

In-Duct/Out-of-Duct Grain Loading (July 15, 1976)

These experiments were designed to determine the amount of particulate which condenses by cooling the flue gas from duct temperature to 250°F, which is the temperature recommended by EPA for particulate sample collection.

The amount of particulate which condensed corresponds to an additional 1.6 gr/scf at the inlet and 1 gr/scf at the outlet. The dry electrostatic precipitator is not able to collect species in the vapor state. The results are summarized in Table 4-16.

During the three in-stack, out-of-stack grain loading determinations (July 15, 1976, 8:50 a.m.-16:30 p.m.), a reddish condensate formed at the inlet tube to the first impinger. This is between the 250°F oven and the first impinger in the ice bath. A sample which accumulated in the inlet pipe was subjected to X-ray fluorescence and SSMS analysis.

TABLE 4-14. GRAIN LOADING DATA INLET

Date	Point	Time	SCF	Grains/SCF
July 10	W 1-12	0640-0845	17.17	1.552
July 10	W 4-6	0908-0923	4.51	.501
July 10	W 1-12	1005-1135	18.59	.519
July 10	E 1-12	0645-0830	19.12	.358
July 10	E 1-12	1010-1230	18.76	.647
July 9	W 1-8	0657-0929	20.91	.647
July 9	W 1-12	1117-1315	18.20	.433
July 9	E 1-5	0650-0852	10.81	.365
July 9	E 1-12	1120-1350	26.51	1.013
July 8	W 1-9	1035-1303	45.33	.422
July 8	E 1-6, 9	1030-1302	28.57	.173
Average Grain Loading				.60

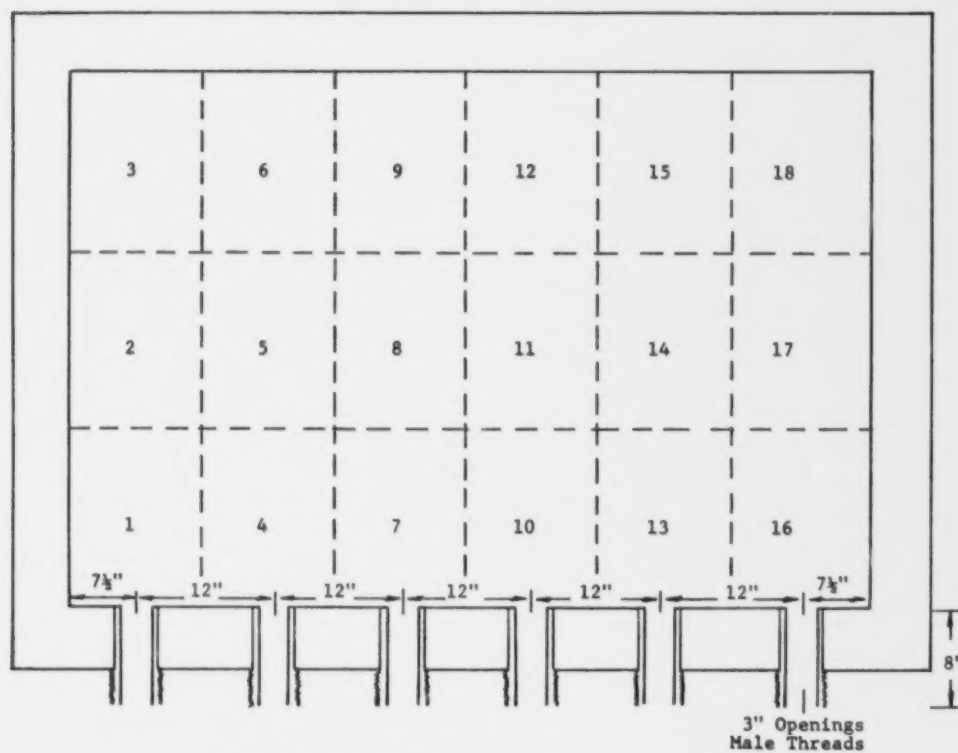
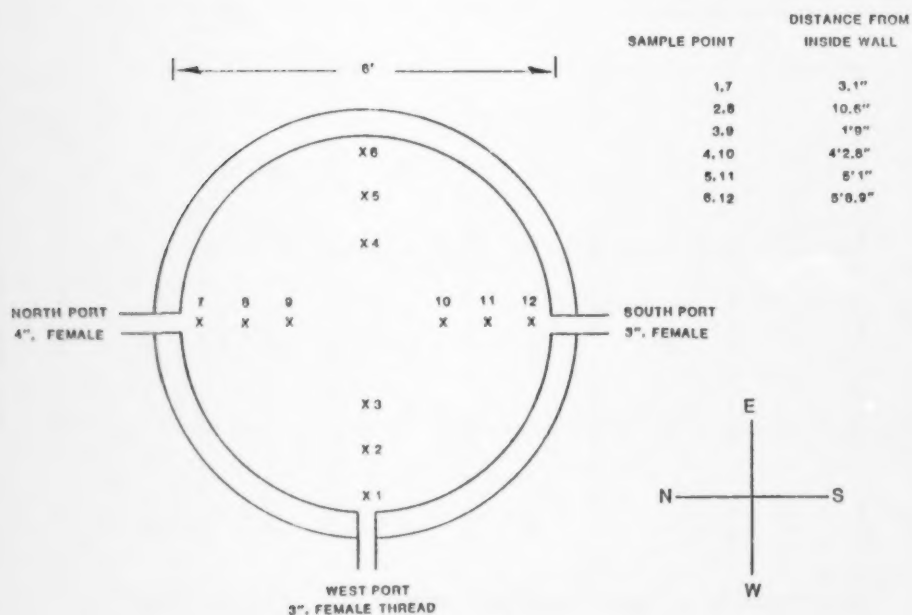
Cross Section and Sample Point Identification at Inlet
East and West Ducts

TABLE 4-15. GRAIN LOADING DATA OUTLET

ESP Outlet	Time	SCF	Grain Loading	Sampling Points
7-10	0630-0814	25.32	.018	W 1-6; S 12-9
	1010-1215	33.05	.017	W 1-6; S 12-7
7-9	0650-0915	25.03	.019	W 1-6; N 7-12
	1135-1315	25.12	.022	W 1-6; N 7-12
7-8	1030-1305	32.88	.025	W 1,2; N 7-12
AVERAGE			.020	



Cross Section and Sample Point Identification of Exit Duct.

TABLE 4-16. IN-DUCT/OUT-OF-DUCT GRAIN LOADING (gr/scf)
(JULY 15, 1977)

INLET					OUTLET				
Run	Time	In-Duct 600°F	Out-of-Duct 250°F	Combined	Run	Time	In-Duct 600°F	Out-of-Duct 250°F	Combined
1	0845-1028	.58	1.89	2.47	1	0850-1020	.027	.94	.97
2	1300-1420	.31	1.25	1.56	2	1300-1400	.072	.78	.84
3	Lost Sample		--	--	3	1530-1630	.019	1.35	1.37

Similar deposits were observed during in-stack grain loading measurements and during arsenic sampling. They also were reported from plant personnel during their effort to determine the arsenic flow rate at the ESP exit.

X-ray fluorescence indicated that arsenic and selenium are the predominant heavy elements in this sample. The presence of smaller amounts of zinc and potentially lead were indicated.

The results of the SSMS analysis confirm the presence of arsenic and selenium as major species (>1000 ppm). Elements found in smaller concentration are lead, rhenium and zinc.

Vapor Train Gaseous Emissions (July 16, 1976)

Compounds emitted as vapors were: arsenic (16 lb/hr), copper (3 lb/hr), fluorine (11 lb/hr) and selenium (2 lb/hr). Arsenolite (As_2O_3) was identified by X-ray diffraction in the condensibles. These emissions found by quantitative analytical methods agree with the X-ray fluorescence analysis and the SSMS results of the material condensed at the impinger inlet tube. The vapor train as described in Section 3 was used to establish these results.

ELECTROSTATIC PRECIPITATOR MATERIAL BALANCE (JULY 11, 1976)

The closure of the material balance results within the calculated error limits increases the confidence in the analytical data and are presented in Table 4-17. Barium and lead were found in the precipitator dust in substantial quantities while the amounts found in the WEP samples collected at the inlet duct were, by comparison low. These results indicate that the use of sulfuric acid in the WEP's as well as the presence of a high SO_3 concentration in the reverberatory furnace off-gases formed lead and barium sulfate precipitates which are not dissolved using the digestion techniques employed. However, the lead concentration found in the exit WEP liquor of 0.6 ppm is below the saturation point of approximately 10 ppm, which was

TABLE 4-17. ELEMENTAL FLOW RATES IN ESP INLET AND OUTLET STREAMS

Element	Inlet (lb/hr)				E in (lb/hr)	Outlet (lb/hr)				precipitator dust	Σ out (lb/hr)	
	Inlet WEP liquor	1st impinger	2nd acid impinger	2nd basic impinger		Outlet WEP liquor	1st acid impinger	2nd acid impinger	2nd basic impinger			
Arsenic	190	.036	.0060	ND	1.8	190±95	140	.0084	.0016	.0055	30	170±84
Barium	ND	ND	ND	ND	ND	<.0085±.005	ND	ND	ND	ND	.023	<.035±.016
Beryllium	.013	1.2x10 ⁻⁷	ND	ND	ND	.013±.006	.011	ND	ND	ND	.00040	.011±.005
Cadmium	.29	.00068	ND	ND	ND	.29±.13	.016	ND	8.1x10 ⁻⁵	ND	.74	.74±.34
Chromium	.027	ND	ND	ND	ND	.027±.012	.011	ND	ND	ND	.018	.029±.007
Copper	56	.0054	.0075	.0086	.018	56±25	1.0	.0055	ND	.0077	.62	63±28
Fluorine	7.4	.23	.029	.021	.0012	7.6±3.2	7.5	.29	.012	.020	.032	7.8±3.4
Mercury	.0011	.0025	.0059	.00066	ND	.010±.006	.00087	.0013	.0027	.00072	ND	.006±.003
Niobium	8.7	.00060	ND	ND	ND	8.7±4.0	.16	.0018	ND	ND	6.6	6.8±3.4
Nickel	.092	ND	ND	ND	ND	.09±.05	.085	ND	ND	ND	.059	.14±.07
Lead	.92	.0023	.00072	ND	ND	.92±.52	.075	.0035	ND	ND	5.3	5.4±2.2
Sulfur	(1320 lb/hr S as SO ₂ , 30 lb/hr in flue dust)			30 lb/hr S as SO ₂ , 30 lb/hr in flue dust		1400±640	(2210 lb/hr S as SO ₂ , 1.2 lb/hr in flue dust)				30	2290±1040
Antimony	.81	9.8x10 ⁻⁵	.00025	ND	ND	.81±.36	.33	ND	ND	ND	1.3	1.6±.80
Selenium	.91	ND	ND	8.6x10 ⁻⁵	.00078	.91±.34	.97	ND	ND	7.2x10 ⁻⁵	.16	1.1±.5
Zinc	.041	.036	.011	.0039	.0081	.099±.046	.0047	ND	ND	.022	.035	.073±.032
	4.3	.0068	.0068	.0033	ND	4.3±2.2	.072	.0064	.0032	ND	4.6	4.7±2.3

determined by adding $\text{Pb}(\text{NO}_3)_2$ to 5% sulfuric acid and equilibrating the mixture overnight. The emission rate of the lead which was found from the WEP outlet analysis is therefore valid. The results of the X-ray fluorescence analysis indicate that at least part of the arsenic and selenium leave the ESP in the vapor state. This is in agreement with the results described under "Gaseous Emissions."

IDENTIFICATION OF MAJOR CRYSTALLINE SPECIES

X-ray diffraction was used to investigate the nature of the major crystalline phases. The goniometer technique was applied. Diffraction patterns from the following samples were obtained:

- reverberatory furnace feed concentrate,
- dust collected by the electrostatic precipitator,
- particulate, collected at the ESP outlet using an in-stack filter,
- condensed particulate - collected at the ESP outlet at 250°F preceded by an in-stack filter at 600°F,
- condensed particulate - collected at the ESP inlet at 250°F preceded by an in-stack filter at 600°F; this filter was unusual in that the collected material was black while that on all other filters used in this manner was very light in color, and
- material which condensed in the glassware following the filter oven during modified EPA Method 5 sampling (in-stack/out-of-stack grain loading).

Copper K_α radiation was used in all diffraction investigations.

A color change on the Gelman filters was observed as function of time. The same observation was reported by Southern Research Institute during Brinks impactor measurement. The presence of CuSO_4 and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in the hopper dust explain these observations. Both compounds pick up water of crystallization upon exposure to water vapor present in the laboratory atmosphere forming copper sulfate trihydrate and pentahydrate. A color as well as a weight change accompany this transition. Both phases were identified by X-ray diffraction on the in-stack filters exposed for several months to laboratory atmosphere.

Arsenolite (As_2O_3) was positively identified in the hopper dust, in the material captured by the in-stack filter, in the deposit on the out-of-stack filter as well as in the impinger operated at approximately 32°F. These findings indicate that arsenolite leaves the ESP in both a solid and a gaseous phase.

Other compounds identified positively by X-ray diffraction are α -Quartz and chalcopryite in the feed concentrate, and probably hematite and tenorite in the hopper dust. The findings of the X-ray diffraction studies are summarized in Table 4-18.

TABLE 4-18. SUMMARY OF CRYSTALLINE SPECIES IDENTIFIED BY X-RAY DIFFRACTION

Sample Designation	α -Quartz SiO_2	Chalcopyrite CuFeS_2	Arsenolite As_2O_3	Copper Sulfate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$	Monatite $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$	Copper Sulfate Pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Hematite $\alpha\text{-Fe}_2\text{O}_3$	Tenorite CuO
Reverberatory Furnace	present	present						
Feed Concentrate (Composite July 12-14)								
Dust Hopper (Composite July 11-13)	present		present	present			probably present	probably present
In-Stack Filter (July 15)			present		present	present		
Out-of-Stack Filter (July 15)			present					
Out-of-Stack Filter (July 15)			present					
Material Condensed in Impinger (July 15)			present					

TABLE OF CONVERSION FACTORS

Multiply English Unit	by Conversion	To Obtain Metric Unit
acres	0.405	hectares
acre-feet	1233.5	cubic meters
barrel, oil	158.97	liters
British Thermal Unit	0.252	kilogram-calories
British Thermal Unit/pound	0.555	kilogram calories/kilogram
cubic feet/minute	0.028	cubic meters/minute
cubic feet/second	1.7	cubic meters/minute
cubic feet	0.028	cubic meters
cubic feet	28.32	liters
cubic inches	16.39	cubic centimeters
degree Fahrenheit	0.555($^{\circ}\text{F}-32$) (a)	degree Centigrade
feet	0.3048	meters
gallon	3.785	liters
gallon/minute	0.0631	liters/second
horsepower	0.7457	kilowatts
inches	2.54	centimeters
inches of mercury	0.03342	atmospheres
pounds	0.454	kilograms
million gallons/day	3785	cubic meters/day
mile	1.609	kilometer
pound/square inch (gauge)	(0.06805 psig+1) (a)	atmospheres (absolute)
square feet	0.0929	square meters
square inches	6.452	square centimeters
tons (short)	0.907	metric tons (1000 kilograms)
yard	0.9144	meters

(a) Actual conversion, not a multiplier.